Polymer-coated inorganic nanocrystals with a defined number of functional groups

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Inorganic hydrophobic nanoparticles of different materials such as Au, CdSe/ZnS, CoPt etc. can be coated with an amphiphilic polymer to yield particles that are stable in aqueous solution.The carboxylic groups on the surface of the polymer shell serve as anchor points for further chemical functionaliziation. Ligand molecules with amino groups can be covalently bound to the particles. Poly(ethylene glycol) (PEG) is an inert biocompatible polymer that is known to decrease unspecific binding of particles to surfaces and to increase the collidal stability at physiological salt concentrations. With bifunctional PEG molecules, the particles can be modified with additional functional groups such as amines, thiols, maleimides etc.By the increase in size, the binding of the PEG molecules to the particles can be monitored by gel electrophoresis and other techniques. If the molecular weight of the PEG molecule is high enough, conjugates of nanoparticles with one, two, and three PEG molecules per nanoparticle can be separated using gel electrophoresis. In this way the PEG molecules act as spacers that allow the sorting of nanoparticles with a discrete number of functional groups, in order to eliminate uncontrolled inter-particle crosslinking in further experiments.

Nanoscale pH-sensing with polymer-coated gold nanorods

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We are reporting on a reversible nanoscale pH-sensor consisting of a gold nanorod covered with the pH sensitive polymer Poly(acrylic acid). This polymer is covalently bound to the gold particle and deprotonats under alkaline conditions. At high pH levels, the PAA backbone is stretched as a result of the repelling forces of the negative charges; additionally, the packing becomes less dense, lowering the refractive index around the particle. This change in the refractive index induces a shift in the plasmon resonance, which is detected with single particle dark field spectroscopy. With such a reversible system, pH variations can be detected at the nanometer scale, which could also lead to the potential mapping of pH landscapes with high precision.

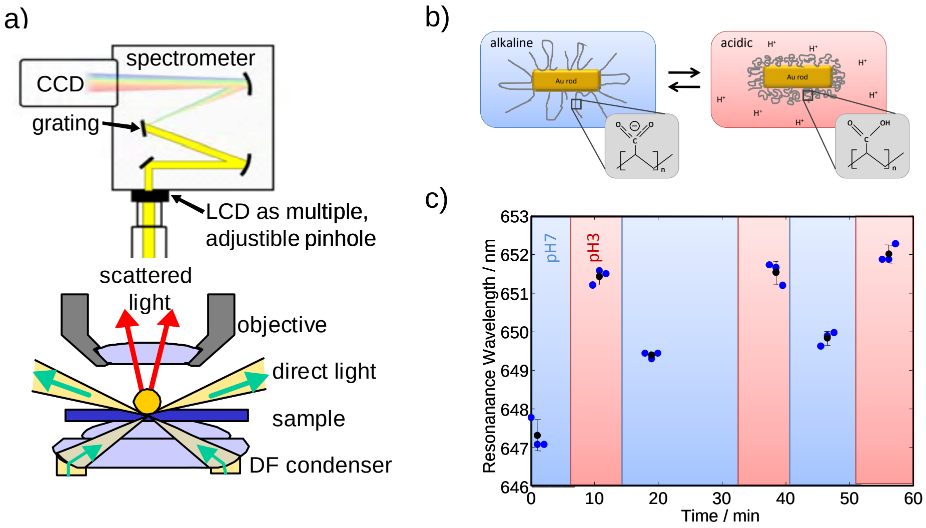

Figure 1a) Schematic view of the darkfield microscope. b) Scheme of the developed pH-sensor. pH is triggering the packing density sensed by the Plasmon. c) Shifting resonance position of one single particle in changing pH conditions.

Probing Nanometre Heights by Fluorescence Lifetime Modulation in Proximity of Conductive Surfaces

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To obtain information from processes and systems, which are too small to be resolved by conventional light microscopy, techniques are required which overcome this resolution limit. Here, we present a method based on the near-field interaction of fluorophores with conductive surfaces, which allows us to precisely determine heights in the range of about 0-50 nm. Fluorophores in proximity of conductors experience, additional to photon radiation, competing de-excitation pathways due to, for example, surface plasmon excitation in the conductor. These mechanisms influence the lifetime of the excited state of a fluorophore and modulate it with a strength that depends on the distance between fluorophore and conductor. We measure distance dependent changes of the fluorescence lifetime of fluorescently labelled microtubules transported by kinesin-1 motor-proteins on a gold surface by wide-field fluorescence lifetime imaging microscopy. We are able to reveal height information in this protein system with precision of about 2 nm.

Surface enhanced fluorescence substrates

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The next generation of molecular diagnostics tools (e.g. microarrays, sequencing systems) are targeted to have single molecule sensitivity. Surface-enhanced fluorescence can be a key enabling factor in achieving this goal. Large-scale arrays of apertured plasmonic structures, in particular, meet the requirements of enhanced fluorescence and background isolation, along with compatibility with existing instrumentation and surface chemistry. The simplest such embodimentis an array of sub-wavelength apertures in a metal film, with which fluorescence enhancement was demonstrated first using Au [1]. Fluorescence enhancement is due to a combination of SPP-mediated excitation enhancement and emission enhancement. Chemical passivation of the Au surface enables standard probe attachment chemistries to be employed at the bottom, glass, surface of the apertures, facilitating real-time detection via background isolation [2]. Even though molecules are confined within holes, the spectral region of enhancement depends strongly on the metal. We have also been working with structures in Al, which provide more balanced enhancement throughout the visible spectrum, opening up a wider range of applications. However, new chemical passivation strategies need to be devised due to the native oxide of Al. Nevertheless, significant fluorescence enhancements can be obtained using commercial two color microarray scanners, consistent with calculations. Tuning of the relative enhancements can be accomplished by adjusting the shape of the apertures. Further, arrays of Al apertures can be produced on microarray substrates using a low cost, volume manufacturing process.

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A New Concept for a Near Field Raman Probe

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The idea to use the localized plasmon of a single metallic particle as a scanning tip for signal enhancement [1] created the new branch of a scanning tip enhanced spectroscopy. The combination of Raman spectroscopy with Scanning Near-Field Optical Microscopy (SNOM) enriches both methods. Raman spectroscopy becomes locally selective, whereas the Raman signal provides a spectral dimension to SNOM, lifting all ambiguities created by the interference between the scattered and exciting light [3].

The standard scheme of tip-enhanced Raman scattering (TERS) with an external illumination of an AFM or STM tip has some disadvantages due to a nonlocal exposure of the sample. We propose the concept of a tip-source. Due to the local illumination, tip-sources lead to a much lower exposure of the whole sample than externally illuminated tips do, whereas the local excitation can be even stronger. In the case of a tip-source the signals are really local and not masked by SERS signals from illuminated areas remote from the tip. Attempts to realise such a scheme by attaching a silver grain to the aperture of a fibre probe gave no appropriate enhancement [4]. We use a metal coated tetrahedral tip (T-tip) [5] for this purpose. A sequential dimensional reduction of an incident beam to surface and edge plasmon modes leads to a local tip excitation equivalent to a dipole inclined at 45^0 with respect to the sample surface [5] as a source for SNOM imaging at a spatial resolution of about 10nm. The presence of z-component of the electric field of such a dipole as well as a local resonance of the metal coated apex of the T-tip are prerequisites for effective TERS with the T-tip [6].

To introduce a new dimension to TERS we propose the concept of a near-field Raman probe. We propose to use the sensitivity of Raman spectra to the local environment, like pH sensitivity of molecules of mercaptobenzoic acid [7]. To test the concept, we covered the T-tip by Raman active molecules of thiophenol, which is non resonant for visible light. A non-resonant near-field Raman probe does not bleach in contrast to fluorescent probes, which degrade fast [8]. Raman spectra measured in contact with a substrate at different locations demonstrated different spectral features while spectra measured sequentially at the same point displayed only a nonlinear response to the excitation intensity. We believe that such an approach can be promising in the investigation of subtle specific interactions on a local scale.

In conclusion we propose two new concepts of near-field probes for more effective TERS measurements and for the use of the TERS signal of the coated tip to monitor local properties of a sample of interest. The efficiency of both concepts was demonstrated experimentally.

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SERS clusters via controlled nanoparticle linking, polymer encapsulation, and small molecule infusion

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Surface enhanced nanomaterials have not been developed into a reproducible system in part due to the difficulty of forming small metal nanoscale junctions in a controlled manner, a necessary requirement for an intense SERS signal given the extreme nanostructural dependence of the phenomenon. We have developed a straightforward strategy for obtaining polymer stabilized SERS-active nanoparticle cluster solutions which act as reproducible substrates to which analyte may be subsequently infused. A central aspect is the development of a kinetically-optimized sacrificial-linking/quenching protocol in which the SERS signal itself is used as the real-time optimization parameter through each surface modification step. The effort is generalized to a solution-based synthesis that is scalable to large-quantity preparation of encapsulated SERS clusters through three stages of linker addition, polymer quenching utilizing low anchor density passivation, and backfilling of the hot spots with analyte (even months later). Clusters were purified, studied in colloidal form under a variety of conditions, embedded in membranes, and applied in cell labeling and uptake studies.

Typically, the cluster distribution of the polymer coated product was shown by TEM analysis to comprise ~ 45% monomers, 25% dimers, 10% trimers, 5% tetramers, and small amounts of larger cluster sizes. Size selective centrifugation was successful for enrichment of the middle weight fraction. Raman correlation spectroscopy in a capillary was used to extract translational and rotation (polarization) diffusion constants, enhancement factors ($>10^7$), Rayleigh scattering, Raman, and continuum background values on a single cluster basis at high throughput. Ag and Au aggregates were compared with core-shell SiO_2-Au nanoshells. The SERS intensity and band ratio histograms from Ag linker-optimized clusters were brightest and more monodisperse than monomers and unoptimized aggregates, and showed rotational anisotropy as expected. Resonant and fluorescent tags are currently being studied on the clusters in context of surface enhanced fluorescence and relationship between Raman and continuum emission.

The surface chemistry of the clusters was explored in well plate format through adsorption and competition studies of various dyes and non-resonant tags. Disulfide, thiolate, amine, carboxyl, phosphine, functional groups and host-guest interactions were tested. Chloride and chemical enhancement effects could be studied in a relatively controlled setting. Sequential addition of two tags resulted in isosbestic-like behavior, suggesting that the total number of available sites in the hot spot is approximately constant, although their infiltration rate through the polymer coating varies. Choice of polymer coating was shown to modulate the Langmuir kinetics and correlated with structure and charge of the functional groups.

Reproducible nanostructured gold surfaces for analytical devices

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Due to their plasmonic properties, nanostructured metallic surfaces are well established in a wide range of analytical fields. One field of application is the surface enhanced Raman spectroscopy (SERS) since the weak Raman process can be enhanced by the interaction of molecules with a nanostructured metallic surface. Classical SERS active substrates like roughened metallic electrodes, metal colloids or evaporated metal layers show a lack of their reproducible SERS response. [1] Recently, it has been shown, that gold nano-diamond SERS arrays produced by electron beam lithography [2] meeting our demands by providing reproducible SERS response across the entire sample area. [3]

Within this contribution different methods for the characterization of gold nano-diamond and gold nano-square SERS arrays and the anisotropic properties of the diamond-shaped pattern are introduced. As a basic and intuitive investigation method far field transmission spectroscopy has been described in the literature. The transmission minima of these patterned samples, characterizing the plasmon excitation, are tuned to the VIS or NIR wavelength range. Additionally these measurements are supplemented by scanning near field optical microscopy (SNOM) investigating the spatial distribution of the plasmon induced electromagnetic fields. [4] These experimental results are verified by means of theoretical calculations. Furthermore, SERS measurements with linear polarized light by rotating the diamond-shaped array in 15 degree steps results in a $\cos^2$ dependency of the SERS signal. [5]

Reproducible SERS substrates may be used in a variety of analytical applications. They may be used as new substrates for a chip-based detection of biomolecules using SERS. The development of a chip-based DNA detection is currently in process. First results of single stranded DNA immobilized on reproducible SERS arrays with and without label show the great capability of these substrates. Furthermore, the application of Raman labels like dyes yields in nearly unlimited multiplexing potential.

Acknowledgements

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Modelling of electromagnetic field enhancement for Ag nanospheres touching Ag/SiO_2 substrates

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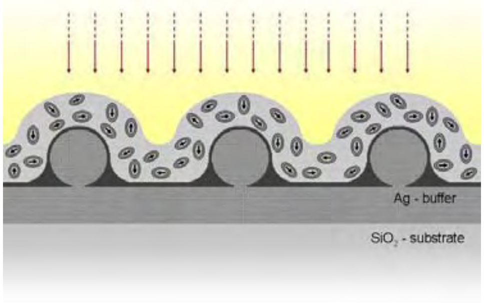
Electromagnetic modelling is a important tool to shed light on the localized surface plasmon resonances (LSPRs) in metal nanoparticles (NPs) and to relate these phenomena to the size, the shape, the composition of the NPs as well as to the surrounding environment.

In this work we theoretically investigate the optical properties of Ag nanospheres on SiO_2 substrate covered by a thin silver layer (see fig. 1): calculations are performed within the Discrete Dipole Approximation (DDA)[1,2] which is an efficient method to compute the absorption and scattering spectra for targets of arbitrary shape and composition.

Until now DDA has been applied to study several target geometries, including metal NPs[3-6] and their aggregates[7] but only few times it has been used to analyse the real contribution of a supporting substrates[8-10]. NPs on semi-infinite substrates are also investigated by using the *Image Dipole Approximation*[11] or using an effective medium approximation in which the dielectric constants of the substrate and of the surrounding background are averaged with the respective weight factors[12]. In cases like the one investigated in this work, i.e. when the silver buffer thickness is less than the above-lying sphere diameter, a complete numerical solution of the Maxwell's equation is required. In this work we discretized jointly the sphere and the underlying substrate by using a box of polarizable points large enough to ensure convergence.

We computed the near-field distribution in proximity of the system using an in house developed routine, and the corresponding local field enhancement trend at increasing distance from the metallic surface: an analysis on the angular distribution of the field intensity around the target was also performed[13]. We put in evidence the role of the silver buffer thickness by changing its thickness.



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Practical aspects for tip-enhanced Raman spectroscopy

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Tip-enhanced Raman spectroscopy (TERS) is a unique tool that provides structural information of surface structures with a lateral resolution on the nanometer scale. When downscaling vibrational spectroscopy to these dimensions not only phenomena related to the high resolution influence the spectra, also great care with respect to probe and sample preparation must be taken [1].

We will show, that in particular the sample substrate preparation for TERS experiments can have a crucial impact on the quality and reproducibility of the results. The requirements for such substrates are manifold – first of all they should provide a flat, if possible atomically flat, support, secondly the possibility to reproducibly immobilize samples is desired and the support should be transparent, as currently the best geometry to illuminate sample and TERS tip is via backscattering through support and sample. We succeeded in the synthesis of micrometersized ultraflat gold and silver crystals with a thickness below 20 nm [2]. At this thickness the metal plates are still transparent and because of their size and smoothness no unwanted localized plasmon effects are to be expected. Additional enhancement effects due to so called gap-modes between the tip and the smooth metal surface, however, should be uniform and can even increase the sensitivity of the system [3]. We will show the first TERS experiments of immobilized bio-molecules on such substrates. Examples currently range from single amino acids to small petides and show the general applicability of this TERS approach towards life science.

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Modeling of metallic nanostructures embedded in liquid crystals. Application to the tuning of their plasmon resonance.

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Purpose

Tuning plasmon resonances of metallic nanostructures has been the subject of many studies recently, both experimentally and theoretically [1-4]. In this work, we theoretically investigate arrays of metallic nanopaticles deposited on a glass substrate and covered by a liquid crystal material (LCM). Extinction spectra at normal incidence are numerically computed using the Finite Difference Time Domain (FDTD) method [5], and we show that by rotating the director orientation around an axis orthogonal to the main direction of illumination, it is possible to tune the resonance of the system.

Methods

The FDTD method is widely used for spectroscopic studies of isotropic structures, but modified recursion equations are required for the description of anisotropic materials and the specific case of liquid crystal structures [6,7].

In this work, we consider periodic arrays of cylindrical gold nanoparticles. They are surrounded by a LCM layer, and we study the influence of the thickness of this layer, as well as the director orientation (measured from the horizontal), on the localized surface plasmon resonance (LSPR).

Results

On the first figure, we have plotted the LSPR wavelengths as a function of the director's orientation for several thickness of the LCM layer (the nanoparticles' height is 50 nm).

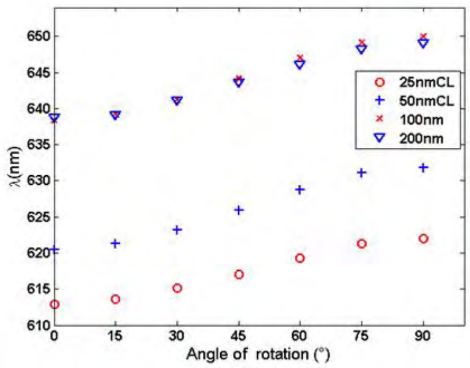
Each curve can easily be fitted by the effective index formula.

$$n = \frac{n_o n_e}{\sqrt{n_e^2 \cos^2\theta + n_o^2 \sin^2\theta}}$$

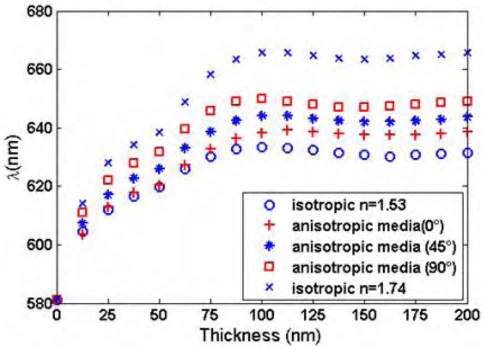
On the second figure, we check the behavior of the LSPR wavelengths as a function of the LCM thickness for three orientations of the director (from 25 to 200nm). Limit isotropic cases are also presented.

Conclusions

Metallic nanoparticles embedded in liquid crystal material exhibit interesting features, as their localized surface plasmon resonance may be easily tuned. The width of the tuning depends on geometrical parameters that may be easily controlled, as well as on the difference $|n_e - n_o|$. This may open the way to new kinds of biosensors or SERS substrate.



LSPR shift as a function of director's orientation.



LSPR shift for several LCM thicknesses.

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A metal coated tetrahedral tip as a probe for tip enhanced spectroscopy

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A tetrahedral glass fragment coated with a 50 nm thick film of gold or aluminum (T-tip) serves as a probe for Scanning Near Field Optical Microscopy (SNOM) [1]. A slightly focused beam, which is directed into the glass body of the tip leads to a highly confined excitation of the metal coated tip apex. The process of light confinement can be considered as a superfocusing of the incident beam by a dimensional reduction of surface plasmon modes where the phase matched excitation of an edge plasmon mode on a metal covered edge plays an important role as a link of the incident beam to the confined tip excitation [2]. The T-tip was used by us for fluorescence SNOM imaging of photosynthetic membrane preparations deposited on a gold film revealing fluorescent features at a resolution of 20 nm [3]. It was further used for Tip Enhanced Raman Scattering (TERS) of thiophenol deposited on a gold film where the TERS signal was mediated by surface plasmon modes of the supporting metal film [4]. We recently demonstrated a new concept of a Near Field Raman Probe [5]. The tip is coated with Raman active molecules and the non resonant TERS signal of the coated tip is used to monitor properties of a surface by their influence on the TERS spectrum of the coated tip. The T-tip is suited as a Near Field Raman Probe because TERS spectra of the coated tip are very stable and can be recorded over a long period of time. Unlike a near field fluorescent probe [6,7], where fluorescent particles or single molecules deposited on a tip serve as a probe, the non resonant TERS signal of the coated tip does not bleach. In order to exploit the full potential of the T-tip for TERS, an internal reflection mode will be attempted where the T-tip serves not only for tip excitation but also for detection of the signal. In the same way as a highly directional beam incident into the tip leads to a confined tip excitation, a dipole placed at the tip apex leads to a highly directional beam of light emitted into the tip. One can thus take full advantage of the mechanism of light confinement by using it for tip excitation and conversely, for signal detection.

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Enhanced fluorescence near dielectric microspheres

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Nanophotonics open new opportunities to increase the emission rate of fluorescent molecules. Using nanostructures such as nanoantennas, metallic nanoparticles or nanoapertures, it is possible to increase both the excitation efficiency (by reinforcing the local exciting field) and the quantum efficiency of the emitters. However, these structures remain complex to manufacture and require expensive nanofabrication facilities.

In this communication, we use polystyrene microspheres as simple and low cost means to enhance the fluorescence signal emitted by single molecules. When a dielectric microsphere is illuminated by a tightly focused Gaussian beam, it over-focuses light in a focal spot whose dimensions are sub-wavelength *in the three directions of space*. In order to experimentally investigate this effect at the single-molecule scale, we use fluorescence correlation spectroscopy (FCS, see Fig. 1). The FCS technique allows to rigorously quantify the fluorescence emission rate enhancement factor. We show that in the vicinity of a 2µm polystyrene sphere, the collected fluorescence signal from Alexa-Fluor 647 molecules is enhanced by a factor of 5. This factor stems from a simultaneous enhancement of the local excitation intensity and of the collection efficiency of the setup.

We also present numerical results to explain the physical origin of the three-dimensional confinement of light brought by a microsphere and give the conditions to obtain a sub-wavelength confinement, i.e. below $(\lambda/n)^3$. The possibilities to couple dielectric spheres with plasmonic structures will be discussed.

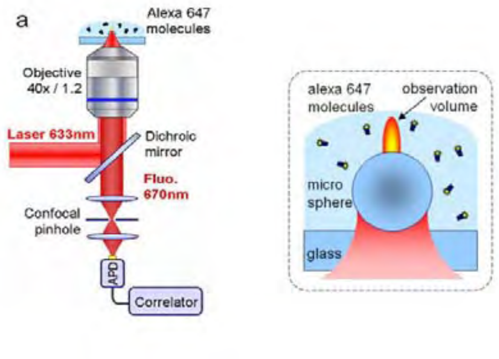

Fig. 1: Left panel: Sketch of the experimental configuration. Right panel: close-up on the microsphere.

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[2] *D. Gerard, J. Wenger, A. Devilez, D. Gachet, B. Stout, N. Bonod, E. Popov, and H. Rigneault, "Strong electromagnetic confinement near dielectric microspheres to enhance single-molecule fluorescence," Opt. Express 16, 15297 (2008).*
[3] *A. Devilez, N. Bonod, J. Wenger, D. Gerard, B. Stout, H. Rigneault and E. Popov, "Three-dimensional subwavelength confinement of light with dielectric microspheres," Opt. Express 17, 2089 (2009).*

Spectral Dependence of Plasmon Enhanced Fluorescence: Separating Excitation and Emission Factors

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We study plasmon-enhanced fluorescence near assemblies ranging from DNA-functionalized metal particles, to quantum dots coupled to silver nanoprisms. We characterize the optical properties of these individual dye/metal and quantum dot/metal clusters using single-particle darkfield scattering, single-particle fluorescence spectroscopy, and single-particle lifetime measurements to quantify the effects of distance and spectral overlap on fluorescence enhancement, quenching and energy transfer. By examining the spectral dependence of the fluorescence enhancement factors and lifetimes we are able to disentangle the varying contributions of emission and absorption enhancement to find different design rules for using plasmonic excitation in applications for photovoltaics, solid-state lighting, and biosensing.

Functionalised Nanoparticles and SERRS for Bioanalysis

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Functionalized nanoparticles have been used in a number of different studies including detection of DNA at ultra low levels, immuno histochemistry and more recently as substrates for surface enhanced resonance Raman scattering (SERRS) based imaging approaches. The advantages of using metallic nanoparticles are that they are very bright in terms of their optical characteristics and also if functionalized in a particular manner to provide a SERRS response give a unique vibrational fingerprint. Here we present the functionalization of gold and silver nanoparticles in such a way that the enhancement effect can be greatly increased through biological recognition and as such effectively turns on the SERRS effect.(Figure 1) This process can give rise to exquisite selectivity in terms of the interaction of the nanoparticles, especially when DNA hybridizations are used and single base mismatches can be analyzed at room temperature. In an advancement of this approach functionalized nanoparticles have also been used as imaging agents for single cells and when functionalized with an appropriate antibody can give back information on the expression of specific receptors on cell surfaces as well as sub-cellular compartmentalization information. Finally in moving away from the *in vitro* applications the functionalized nanoparticles can be modified in such a way that they are active *in vivo* and preliminary data relating to *in vivo* studies of imaging and therapeutic uses of functionalized SERRS active nanoparticles will also be presented. This presentation covers the full range of design, the optical properties and finally the biological properties of functionalized nanoparticles in relation to specific disease states.

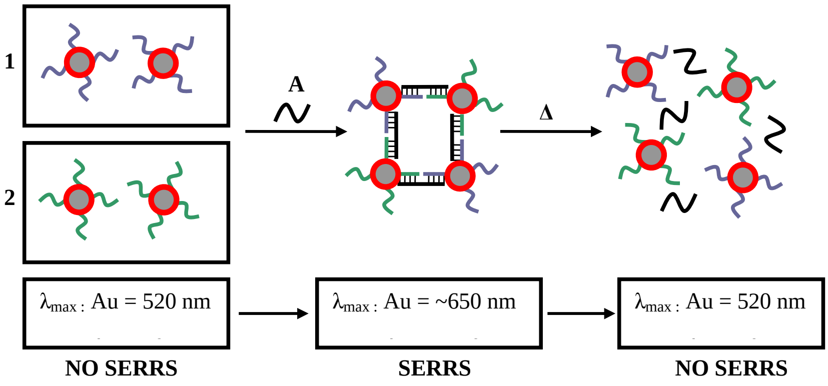

Figure 1. Schematic representation of the melting transition of DNA-nanoparticle conjugates. Two sets of nanoparticles are functionalised with different sequences, non complementary to each other (1, 2). A target complementary to both (A) is introduced and the conjugates hybridise, resulting in a shift in surface plasmon. Upon heating the DNA duplex denatures and the plasmon returns to its starting value.

Vacuum Rabi splitting and strong coupling dynamics for surface plasmon polaritons and Rhodamine 6G molecules

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We report on strong coupling between surface plasmon polaritons (SPP) and Rhodamine 6G (R6G) molecules, with double vacuum Rabi splitting energies up to 230 and 110 meV. In addition, we demonstrate the emission of all three energy branches of the strongly coupled SPP-exciton hybrid system, revealing features of system dynamics that are not visible in conventional reflectometry. Finally, in analogy to tunable-Q microcavities, we show that the Rabi splitting can be controlled by adjusting the interaction time between waveguided SPPs and R6G deposited on top of the waveguide. The interaction time can be controlled with sub-fs precision by adjusting the length of the R6G area with standard lithography methods.

SERS on lithographic substrates: polarization effects and spectral enhancement factors

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[1] MacDiarmid Institute, School of Chem. Phys. Sci., Victoria University of Wellington, New Zealand
[2] Laboratoire ITODYS, Universite Paris 7, Denis Diderot, Paris, France
[3] Institute of Physics, Karl Franzens University Graz, Austria

Regular arrays of quasi identical gold nanoparticles of controlled shape, as fabricated by electron beam lithography, are an important platform for systematic research on SERS phenomena. They allow to design the far- and near field properties and show uniform but moderate enhancement factors without hot-spots [1]. With the help of such gold-nanoparticle arrays, we could experimentally verify the generalized electromagnetic theory of SERS beyond the $|E|^4$ approximation [2]. As a consequence of this concept, an almost complete polarization rotation of the SERS signal with respect to the incident polarization can occur for prolate nanoparticles [3] (Fig. 1). Another aspect we could demonstrate, is the spectral variation of the SERS enhancement factors [4], related to the surface plasmon resonance positions.

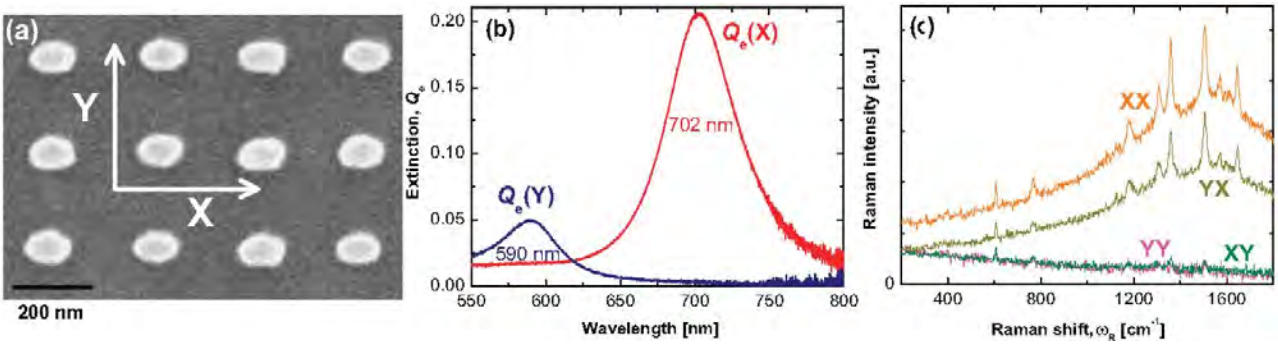

Fig. 1: (a) SEM image of an array of prolate gold nanoparticles. (b) Extinction spectrum of the array for X- and Y-polarization. (c) SERS spectra for the four excitation-detection polarization configurations.

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Modelling of optical properties and temperature distribution in and around Gold nanorods

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Abstract: Pulsed laser irradiated gold nanoparticles can be used to modify or destroy cells and proteins. In contrast to spherical particles, it is much more difficult to destroy cells with nanorods and pulsed irradiation. Calculations of absorption and temperature and transient absorption measurements show a strong transient bleaching, which explains the strongly reduced efficacy of nanorods.

Introduction

Rod shaped gold nanoparticles permit a shift of the optical absorption maximum into the red and near infrared spectral range between 700 and 1100 nm – the optical window of tissue, where a medical use of the particles is possible. For optimizing medical applications, optical properties of gold nanorods were calculated by electrostatic approximation assuming elliptical shape. A semi-analytical model was used further to calculate the laser induced temperature development inside and around the particles. Transient absorption measurements were carried out under nanosecond pulsed irradiation in order to confirm calculations.

Methods

Temperature distributions in and around the nanoparticles were calculated by a (semi-) analytical model. The model permits the calculation of the temperature response to a real measured laser pulses. The optical absorption cross-sections of the nanorods were calculated with the help of the electrostatic approximation for ellipsoidal particles. The results of the temperature modeling and calculation of optical properties were confirmed by steady-state and transient absorption measurements.

Results and discussion

By calculations and measurements three energy ranges, governed by different physical effects on the particle absorption, were determined: In the lowest range transient bleaching of the LSPR band occurred. Due to the large absorption efficiency at the LSPR peak wavelength, sufficient heat is generated within the particles that the surrounding water evaporates. The decrease in refractive index causes a LSPR band shift into the visible wavelength range, while the absorption at the irradiation decreases. At higher radiant exposure, calculations predict a temperature increase of 600 K in the particle lattice and 300 K in the interface layer (on particle surface) during the first 500 ps of the irradiation pulse. Though, after the onset of cavitation the transient LSPR peak bleaching reduced absorption to less than 2 % of the primordial efficiency, residual absorption leads to particle melting, because the bubble isolates the particle. TEM images of irradiated samples showed partial melting resulting in deformed and odd shaped rods. Additionally, in UV-VIS spectra taken after irradiation the loss of the characteristic LSPR absorption band was observed, while the absorption characteristic of spherical particles increased. Thus, in the medium irradiation range transient as well as permanent bleaching of the LSPR band is observed. With further increase of radiant exposure the fraction of particles, which exhibits transient bleaching and undergo melting, grows.

Conclusion

Temperature calculations and experiments have shown an extreme sensitivity of the LSPR peak position to a bubble formation, leading to transient bleaching during irradiation. The rapid shift of the LSPR peak position already limits the effects on cells. Thus, for the application of nanoparticles assisted laser inactivation of cells or proteins, the energy deposition is limited strongly, whereas neither the thermal nor the mechanical destruction radius can develop sufficiently. Different methods to compensate the sensitivity of the absorption band will be investigated in the near future as well as the use of alternative systems such as "core-shell nanoparticles".

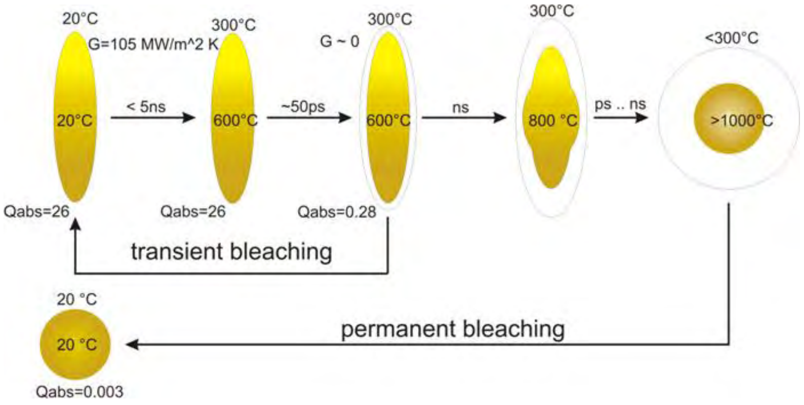

Figure 1: Model for the temperature increase, absorption and particle shape change during the nanosecond pulsed irradiation

Optical sensors by nanoholes with nanoparticles

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Requirements for optical sensors in bio-analytical applications are a high sensitivity, low background and high resolution. The standard method in bio-analytics is fluorescence labeling, possibly in combination with different measurement techniques (FLIM, TIRF, etc.) for the detection of bio-molecules. A whole new class of labeling approaches based on metal nanoparticles has been developed in the last decade. Here we propose the use of noble metal nanoparticles as labels in nanoholes. On one side noble metal nanoparticles are very stable, can be bio functionalized and have (due to the localised surface plasmon resonance LSPR) a high optical signal that can be detected by optical microscopy. One the other side nano scale holes show the potential for especially paralled sensor applications due to their small size and their defined position. One basic principle is hereby the change of refraction index in LSPR – systems, another is the enhanced transmission through the nanoholes [1]. The combination of nanoholes and nanoparticles leads to increased signals through the optical properties which can be used for optical detection of bio analytes. Therefore the integral optical properties of nanoholes filled with nanoparticles were investigated with different methods and compared to empty holes. For characterization of the exact number of particles in the holes Atomic Force Microscope and Scanning Electron Microscope were used. The spectroscopic measurements were conducted with an optical microscope with a coupled spectroscope. The goal is the application of nanoparticles as marker for biomolecules [2,3] in order to use the novel optical signal from nanoholes with nanoparticles for detection [4] of bio molecules. The detection is realized by simple optical readout. This method offers highly parallel and sensitive detection down to single nanoparticle labels.

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DNA-Nanoparticle Conjugates constructed with DNA-loops

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Noble metal nanoparticles commonly exhibit narrow adsorption/scattering peak in the visible part of spectrum caused by the localized surface plasmons (LSP). The resonance frequency of LSP depends on the size of the particles and the permittivity of the surrounding medium [1]. Binding events in close vicinity of such nanopartcle will therefore lead to a change in the LSP resonance frequency; several designs of biosensors using this effect were suggested recently (see for example [2]). When a metal nanoparticle is placed in close proximity to a metal film, LSP in the nanoparticle can couple to the surface plasmon polaritons (SPP) in the metal film. The interaction between the SSP in the metal film and LSP in the nanoparticles depends critically on the nanoparticle-film distance [3].

Gold nanoparticles have been the far most used noble metal nanoparticles, mainly due to their relatively high stability. However, in comparison to gold, silver nanoparticles offer a range of advantages, including a higher sensitivity due to a narrow LSP peak and the possibility to use metal surface enhanced fluorescence to name a few [4]. Unfortunately, the modification techniques for silver nanoparticles are not as well elaborated as those for gold nanoparticles. In this work we achieved stabilization of bare silver nanoparticles using hairpin-structured DNA molecules with the phosphorothiolated hairpin area. The binding of hairpin DNA to silver nanoparticles can be observed as a red shift and a broadening of the surface plasmon peak of the nanoparticles (see Fig 1). The particles acquire negative charge due to the attached DNA molecules and are stable at least on a scale of several weeks. Gel electrophoresis confirmed binding of DNA molecules to the nanoparticles: DNA stabilized silver nanoparticles formed a well defined band in the gel, while the non-modified silver nanoparticles couldn't enter the gel.

We believe that this type of DNA-Ag nanoparticle construct offers unique possibilities for measuring the coupling of LSP and SPP providing a well defined separation between the nanoparticles and the metal film. Moreover this construct could be used to measure electrical transport through short DNA segments. We will present some preliminary data covering these areas of research.

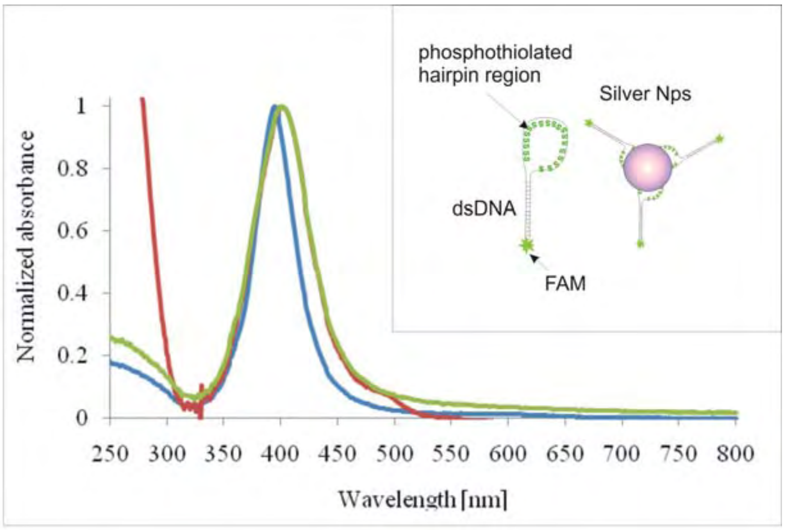

Figure 1: Absorption spectra of silver nanoparticles (blue) and silver nanoparticles with bound hairpin DNA before (red) and after (green) centrifugation. The spectra are normalized at the maximum value of the surface plasmon peak, which is observed around 400nm.

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Nanoplasmonic molecular sensing

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Label-free molecular detection based on plasmons in metal nanostructures can utilize several different principles, the most important being surface-enhanced Raman scattering (SERS) and refractive index contrast. In this presentation, some of our recent achievements in these two areas will be discussed.

Biosensing based on the refractive index sensitivity of surface plasmons is still the most influential and widespread application area in plasmonics. Traditional sensing schemes based on surface plasmon polaritons in flat gold films, so-called Surface Plasmon Resonance (SPR) sensing, has been developed and commercialized since the 80's while sensing schemes based plasmons in nanostructured metals, so-called Localized Surface Plasmon Resonance (LSPR) sensing, is more recent. However, the actual pros and cons of the two methodologies, in terms of sensitivity and other critical parameters, are poorly understood. We have now performed direct comparisons of the two sensing techniques using the same illumination and detection conditions [1]. It was found that the SPR sensor is outstanding in bulk sensitivity, as expected from theory as well as previous reports. However, for biosensing measurements, the slightly larger plasmon shifts observed for SPR come with a drawback of additional noise compared to LSPR sensing performed at the same resonance wavelength and otherwise equal measurement conditions. The difference in noise levels are particularly notable compared to LSPR sensing in reflection mode, which produce a significantly a lower detection limit than the SPR sensor.

Aggregation of metal nanoparticles strongly affects their optical response, including the magnitude of induced fields, position and width of localized plasmons. A particularly important example of this near-field coupling effect is SERS, which is typically strongest for molecules situated in gaps between interacting particles. Hence, control of the aggregation state of metal nanoparticles is a prerequisite for bio/chemo sensors based on SERS and other surface-enhanced spectroscopies. Here, we use optical tweezers to trap, aggregate and manipulate colloidal Ag nanoparticles for the purpose of lab-on-a-chip based SERS sensing [2]. The Ag colloid and the Raman probe solution were injected separately from two input tubings and mixed at a cross before flowing through the microfluidic channel, where Ag nanoparticles were trapped by a NIR laser and generated an intense SERS signal (Fig. 2(a) and 2(b)). Elastic scattering spectra showed a red-shift during a trapping process and a blue-shift while the trapping laser was blocked (Fig. 2(c)), demonstrating near-field coupling due to optical aggregation.

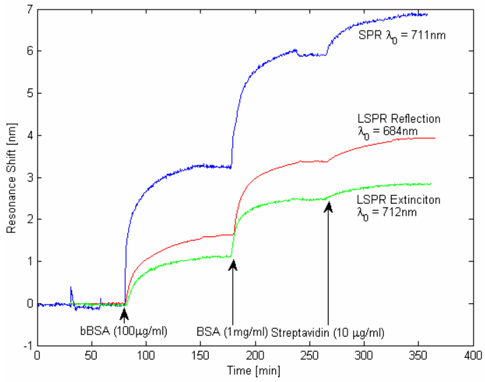

Figure 1: Biomolecular adsorption kinetics as measured by the shift of the plasmon wavelengths as molecules are inserted into the flow cell. SPR sensing was performed using fixed angle white light illumination in Kretschmann geometry for gold films with thickness ~50 nm on glass. The LSPR sensor utilized layers of gold nanodisks made by colloidal hole mask lithography.

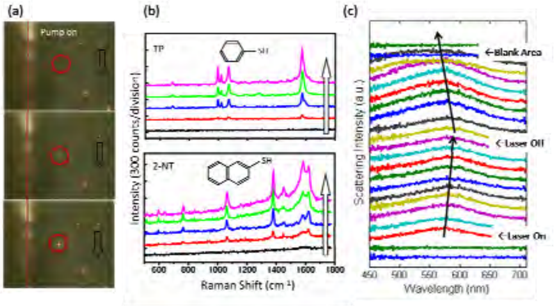

Figure 2: (a), (b) Dark-field (DF) images and temporal SERS spectra recorded during a trapping process in a microfluidic channel. (c) DF scattering spectra measured during trapping between two glass slides.

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Gold nanosensors based on one- and two-photon surface-enhanced Raman scattering

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Gold nanoparticles show favorable properties for spectroscopic applications due to their surface plasmons. The presence of local optical fields in their close proximity enables the generation of a high enhancement of excitation light and emitted or scattered photons. Gold nanoparticles and their aggregates can be used as efficient substrates for surface-enhanced Raman scattering (SERS) and also surface-enhanced hyper Raman scattering (SEHRS). We have constructed a number of different types of nanosensors for bioanalytical applications based on the SERS/SEHRS signals from molecules in the proximity of gold nanostructures and will report on the characterization and application of these sensors in complex systems such as biological cells. The gold nanoparticles for SERS enhancement were generated by different methods, bottom-up in chemical reduction processes, but also top-down, by laser ablation from gold foils. The latter process yielded particles and nanoaggregates with very good enhancement factors, as predicted by theory [1], and surface properties that enable measurements at low analyte concentrations due to lack of any background signals from other molecules at the particle surface [2]. The delivery of nanoparticulate SERS substrates into a system-to-be-analyzed has to be adapted to the morphology and ultrastructure of the sample. We synthesized gold and also silver nanoparticles inside sporopollenin, a biopolymer of unknown chemical and ultra-structure, the constituent of the outer shell of pollen grains. The gold nanoparticles were characterized regarding morphology as well as regarding their plasmonic properties. The in situ generated nanostructures can be used as substrates for SERS and deliver SERS spectra from the so far unknown sporopollenin polymer [3]. This puts into perspective the molecular characterization of sporopollenin by vibrational spectroscopy, a task that was so far unsolved for many sporopollenin species due to high and broad fluorescence and weak signals.

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[3] V. Joseph, U. Panne, J. Kneipp, submitted

PRODUCTION AND OPTICAL PROPERTIES OF DNA-NANOPARTICLES HYBRIDS

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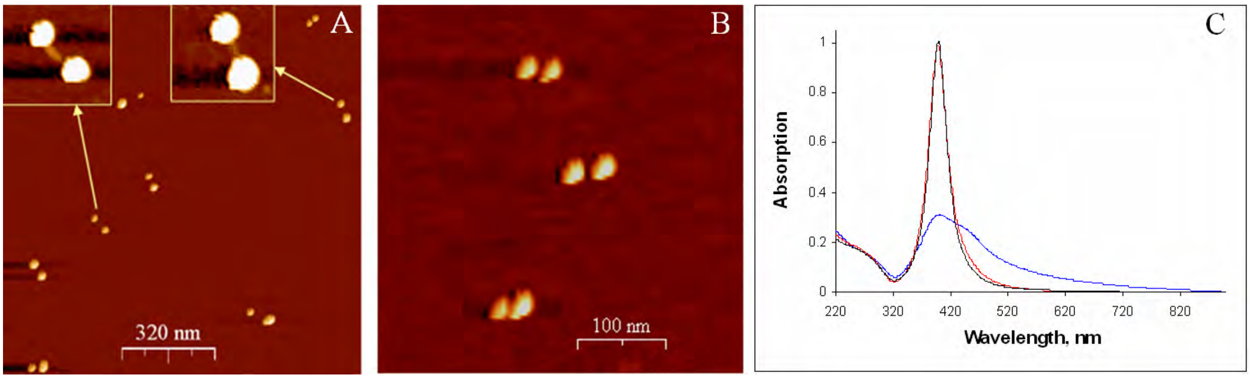
We have shown that phosphorothioated residues are capable of specific interaction with gold surfaces (1) and with silver and gold nanoparticles. This property of the phosphorothioated residues was used to connect two silver nanoparticles to the opposite ends of the double stranded DNA. The double stranded poly(dA)-poly(dT) homopolymer containing 5 phosphorothioated residues at both 5' end of the DNA was synthesized using enzymatic procedure developed by us earlier (2). Incubation of the DNA with molar excess of silver particles (10-20 nm in diameter) yielded DNA-nanoparticles hybrids shown in the figure. Figs A and B present AFM images of nanostructures composed of a pair of spherical silver nanoparticles connected to the opposite ends of a 150 and 30 base pairs double stranded poly(dA)-poly(dT) respectively. As seen in Fig. C the shape of the absorption spectrum of the silver particle dimers depend strongly on the interparticle distance. The absorption spectrum of the particles connected by 150 base pairs DNA (red curve in Fig. C) is similar to that of the monomer particles (black curve in Fig. C). This suggests that no plasmon coupling occurs between the particles separated from each other by approximately 50 nm. Reduction of the interparticle surface-to-surface separation distance in the dimers to less than the particle size leads to a broadening of the spectrum and a decrease in the intensity of the absorption at 400 nm (compare black and blue curves in Fig. C). This indicates that there is strong plasmon coupling between the silver particles linked by 30 base pair DNA.



AFM topography image of pairs of silver nanoparticles connected by to 150 (**A**) and 30 base pairs (**B**) poly(dA)-poly(dT) labeled by phosphothioated residues at both ends of the DNA. **C-** Absorption spectra of the monomer particles (black curve) and particles linked by 150 (red curve) and 30 base pairs (blue curve) poly(dA)-poly(dT).

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How to find the optimum plasmonic resonator for the sensing of single biomolecules and dielectric layers?

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The spectral position of the plasmonic resonance of metal particles is highly dependent on the dielectric properties of the resonators surrounding. Therefore, changes in the dielectric response can be detected as spectral shift as sketched in Fig. 1a in different spectroscopic schemes. Based on this effect, plasmonic resonances can be used as chemo- or biosensors. The ultimate goal in this context would be the label-free detection of the binding and unbinding of an individual biomolecule to an individual resonator [1]. In order to further push the detection limit towards such single molecule sensitivity, a systematic optimisation of material, size and shape of the plasmonic resonator must be done.

We first perform a theoretical analysis of the sensitivity of plasmonic sensors [2]. We distinguish three typical model analytes, changes in the bulk refractive index (a), growth of dielectric layers (b) and attachment of nanometer sized spheres (c). These concepts are illustrated for the crescent-spaped resonators sketched in Fig.1. Different design criteria apply, depending on the type of analyte and dominating noise. In particular we discuss the applicability and limitations of the Figure of Merit (FOM) for particle sensitivity that has been discussed in literature[2].

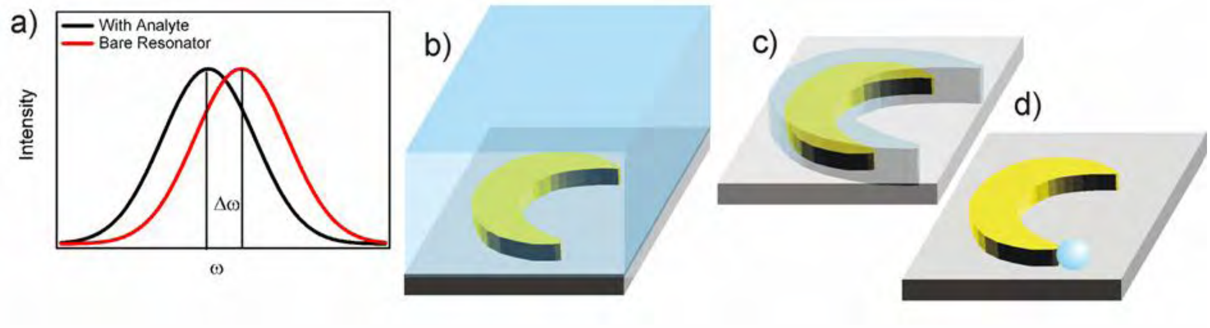

Fig. 1: a) sketch for a resonance shift. b) Crescent-shaped resonator immersed in bulk dielectric. c) coating with a layer. d) Attachment of a dielectric sphere.

Experimentally, crescent-shaped metal particles are studied as an example. Their response to the attachment of thin layers [3] as well as dielectric nanoparticles [4] is investigated to support the theoretical analysis. For the latter experiment, 60 nm polystyrene colloids were used a model analytes which could be manipulated with an AFM-based nanomanipulation tool, see Fig. 2 for a sketch. Based on these experiments the resonance detuning upon attachment of a confined analyte could be investigated with full control over the experimental geometry, providing detailed information about the near field on a scale of 10 nm. Extrapolation to the typical dimension of biomolecules suggests that label-free single-molecule spectroscopy with plasmonic resonatorsis feasible.

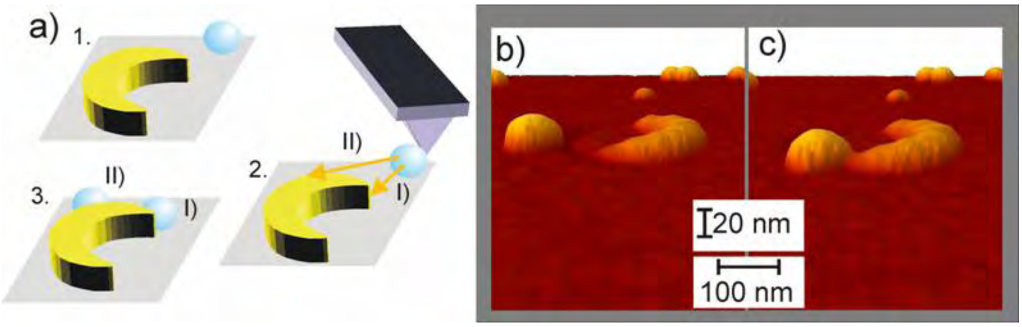

Fig. 2: a) Cartoon illustrating the attachment of a dielectric sphere to a gold crescent by AFM nanomanipulation. b,c) Crescent and Sphere before and after attachment as seen in the AFM.

[1] J. N. Anker, W. P. Hall et al. Nature Mat. 7, 442-453 (2008)
[2] A. Unger, M. Kreiter, submitted January 14, 2009
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Optical resonances of metallic sphere-on-plane geometries and their potential for fluorescence enhancement

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Plasmonic sphere-on-plane resonators are constituted of noble metal spheres with typical diameters of 50-100 nm, separated from a metal surface by a very thin gap of 0.5-3 nm. They exhibit optical resonances with tremendous enhancement of the electrical field within the nanometer-sized gap and are therefore among the most efficient structures for the concentration of light to small volumes.
Although sphere-on-plane resonators were among the first structures to be discussed in the context of enhanced spectroscopies [1,2]. The quantitative description of real structures should take into account the geometrical imperfections suggested in Fig. 1a) as well as corrections to bulk electromagnetism on the very small length scales under investigation.

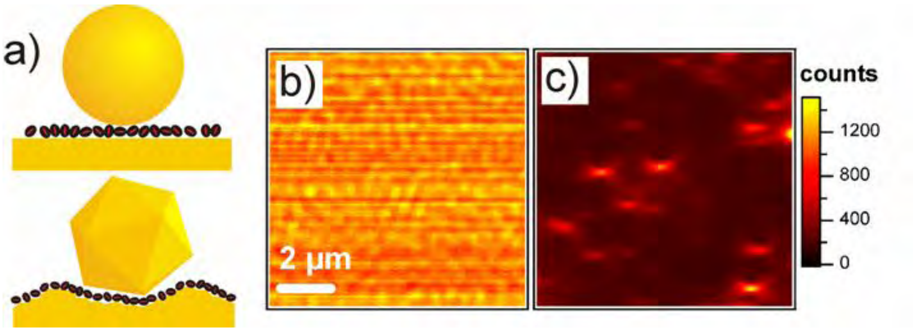

Fig. 1: a) Sketch of an ideal sphere-on-plane geometry as assumed for modelling (left) in comparison to a realistic sketch, taking into account crystallinity of the metal colloid and the typical roughness of a metal film (right). b) Colloid-decorated gold surface seen with standard (left) and plasmon mediated dark field microscopy (right)

The use of different molecules as spacer for the formation of the gap allows us to vary the gap width systematically. In particular, fluorophores are placed in the gap by using large dendrimer molecules with a defined, rigid three-dimensional structure as spacers[3]. Of particular interest is the possibility to build the dedrimer around an organic chromphore and thus combine two functions in one molecule.
We have developed a method to characterise ensembles of sphere on plane resonators using the detuning of the propagating surface plasmon [3]. For the investigation of individuals, 'Plasmon-mediated dark field microscopy' [4] has been implemented allowing for the determination of single-object scattering cross sections with high accuracy. Fig. 1b and c show a comparison of sample with sphere-on-plane resonators which remain invisible when imaged in a classical dark-field mode (b) but are easily seen in plasmon-mediated dark field microscopy (c).
To model the resonance wavelength of sphere-on-plane resonators, both the thickness and the dielectric response of the spacer layer must be specified. We determined these two quantities without any adjustable parameters and found a remarkably good agreement of the simple sphere-on-plane model with the experimental ensemble values [5].

The fluorescence of a the organic dye perylene-diimid which is incorporated in the spacer layer is strongly enhanced by the resonance, silver being more efficient than gold. We observe significantly modified emission spectra beyond a simple convolution of the free dye emission and the particle resonance.

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Microintegration of plasmonic nanoscale objects using dielectrophoresis for nanophotonic application

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Dielectrophoresis (DEP) describes the behaviour of polarizable objects under the influence of an AC-field. It is a valuable tool for the integration of micro- and nanoscale object in an existing (Fig. 1) microelectronic environment. Therefore this technique connects bottom-up nanoscale objects to top-down technical periphery like microelectrodes from classical photolithographic process is possible. It was demonstrated that the integration and separation using discrete DEP parameters with different sized gold nanoparticle could be accomplished (Fig. 2). This offers a great potential for nanoparticle assembling and sorting application. In addition it was also possible to form high conductive nanoscale bridges between two electrodes and characterize those assembled wires by V-I characteristic (Fig. 3). Furthermore, switching of nanosized structures e.g. gold nanoparticles, silicon nanowires and DNA could be demonstrated (Fig. 2-4).

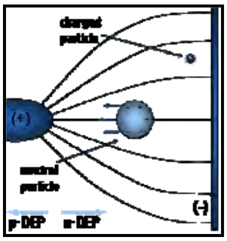

Fig.1: Principle of DEP

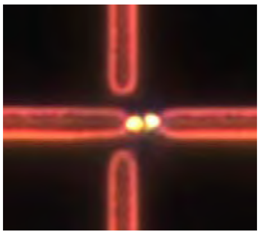

Fig. 2: Conductive bridge made from 30nm gold nanoparticle (R<1000Ω)

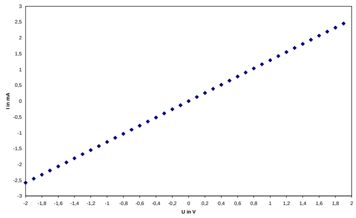

Fig. 3: V-I characteristic of 30 nm gold nanoparticle bridge

Fig. 4: Single silicon nanowire trapped between electrodes

Plasmon Resonance Enhanced Absorption and Circular Dichroism

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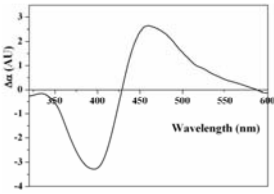
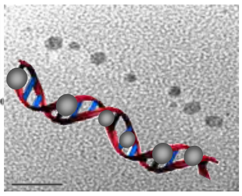
Colloidal Ag nanoparticles coated with L-glutathione attached to a bimane chromophores were studied by absorption, circular dichroism (CD) and fluorescence spectroscopies. The absorption and CD were resonantly enhanced via Ag surface plasmons by two orders of magnitude. The wavelength and particle size dependence of the enhancement indicated that the electromagnetic "antenna" effect was in action, as found in other surface enhanced optical phenomena. Preliminary results for other systems will also be presented.





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Small metal nanoparticles as excitation energy transfer acceptors: the microscopic mechanism unraveled by quantum mechanics

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Metal nanoparticles are able to electromagnetically interact with nearby chromophores to strongly affect the chromophores optical properties. Among other effects, MNPs have been investigated (both experimentally and theoretically) as highly effective acceptors in Excitation Energy Transfer (EET) applications. The current understanding of MNP effectiveness in EET is that the process involves the excitation of the MNP surface plasmons. In fact, surface plasmons have unusually large transition multipoles, and thus are able to enhance the phenomena involving electromagnetic fields. Surface plasmons are available excitations for the MNP as long as the response of the MNP electrons remains metallic in character. However, the confinement of the metal electrons in increasingly small particles causes the transition from the metallic behavior to well-defined electron transitions as found in molecules. Small MNPs (SMNPs), having sizes < 2 nm, represent the bridge between metallic and molecular systems. Therefore, the study of SMNP is the key to understand the transition between the MNPs behavior and that distinctive of “usual” molecule. EET involving MNPs is currently described on the basis of continuum dielectric theories that employ empirical bulk dielectric permittivities. On the contrary, SMNP are small enough to be treated by first principle quantum mechanical approaches. Therefore, the unbiased microscopic behavior of the system can be unraveled by this method, providing important new insights.

In this talk, we report an ab-inito quantum-mechanical study of the EET[1] between a typical chromophore ((*N*,*N*'-dimethylperylene-3,4,9,10-dicarboximide or perylene diimide, PDI)) and a gold SMNP (Au_{20}), as a function of their relative distance and orientation. By comparing the QM results with those obtained for a hypothetical nanoparticle that conserves bulk gold dielectric response (and thus sustains surface plasmons),[2] we show that the molecular-like Au_{20} is intrinsically as effective in accepting excitation transfer as the hypothetical plasmon-sustaining gold nanoparticle once shift of the absorption bands are taken into account.

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Quantum-mechanical study of the excitation energy transfer to metal clusters

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In the last years, the role of metal nanoparticles (MNP) as effective acceptors in excitation energy transfer processes has been largely analyzed from an experimental [1] and theoretical point of view [2]. The current understanding of the effectiveness of MNPs in optical phenomena is that the processes involves the excitation of the MNP surface plasmons.

In this work such an interpretation is analyzed using an ab-initio quantum-mechanical description of the energy transfer process between a typical chromophore (perylene diimide, PDI) and different metal clusters (Au_{20} and Ag_{20}), as a function of their relative distance and orientation.

The QM values of the EET rate between PDI (the donor D) and the metal cluster (the acceptor A) have been obtained in the weak coupling limit, by applying the Fermi Golden Rule:

$$k^{EET} = \frac{2\pi}{h} V^2 J$$

where *J* is the spectral overlap defined with respect to area normalized donor emission and acceptor absorption spectral line shapes and *V* is the electronic coupling between D and A. Both *J* and *V* are here obtained using the DFT formulation of the response function approach, also known as Time Dependent Density Functional Theory, TDDFT. In the model we have developed [3], TDDFT transition densities of the donor and the acceptor are used to calculate the Coulomb contribution to the coupling without reverting to any multipolar approximation and, at the same time, including electron exchange and correlation contributions.

By comparing the full QM results with those obtained for a hypothetical nanoparticle that conserves bulk metal dielectric response, the role of surface plasmons is analyzed together with the effects of the quantum-size blue-shift in the metal absorption maximum.

In addition, we have tested the effects of a surrounding environment, that is, the screening effect in the electronic energy transfer process due to the solvent.

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Near field study of nano-antennae by photochemical imaging

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Purpose

We study experimentally and theoretically the optical near-fields produced by complex metal nano-antennae under a variety of illumination conditions through photochemical imaging [1]. The method relies on the optically induced vectorial molecular mass transport of a light sensitive copolymer. The experimental and theoretical results clearly show that this method can map the three spatial components of the optical near-field of complex metal nanostructures.

Methods

Metal nanostructures were fabricated by electron beam lithography through the lift-off method. The azo-dye molecule-containing polymer consists of the azo-dye molecule Dispersed Red 1 (DR1) grafted as a side chain to PMMA in a 30% molar ratio (DR1MA/MMA). DR1MA/MMA is then dissolved in 1,1,2-trichloroethane and spin coated onto the nanostructures. AFM measurements show that after spin coating the metal structure, the DR1MA/MMA film is about 100 nm thick, with 50 nm above the nanoparticles. Irradiation of the sample is performed at normal incidence relative to the sample using a green laser line (514 nm or 532nm). Calculations of the obtained topographies are obtained using a Monte Carlo method based on a statistical model we developed [2].

Results

The method was applied to map the electromagnetic near-field of silver bowtie nanostructures or nanowires. In particular, in the case of the bowtie we find that longitudinally polarized plasmons are confined at the top of the metallic structures (see figure 1). Furthermore, the intricate optical near-fields in the polymer lead to molecular trapping regions at intensity minima [3].

The statistical model-based Monte Carlo method shows good agreement with far-field and near-field observations. Using the complex calculated electromagnetic field, we mimic the experimentally obtained topography showing the predictive aspect of our model.

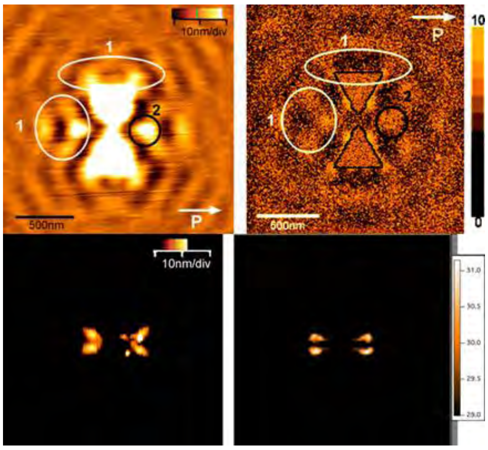

Figure 1. Images of the sample surface after irradiation. The polarization is perpendicular to the major axis of the bowtie. (a) and (c) were obtained by AFM and (b) and (d) are the corresponding calculations.

Conclusions

We show that our method of photochemical imaging allows for mapping the optical near field of complex metal nanostructures. Moreover, we show that the model we developed is a very good predictive tool allowing us to numerically map the expected topographies induced by photoactivated molecular mass motion.

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Probing Ribozymes Folding Pathways Using Gold Nanorod Based NSET Ruler

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Ribozymes, cellular RNA molecules that catalyze chemical reactions, have fundamental implications for the evolution of life on the planet and provide insight into biocatalysis in general. Like protein enzymes, they must fold into a conformation that provides a local environment in which catalysis can proceed. RNA folding is a remarkably complex problem that involves ion-mediated electrostatic interaction, conformational entropy, base pairing and stacking, and noncanonical interactions. Here we will discuss our recent effort on developing gold nanomaterial based NSET Ruler [1-6], which can be used for probing the transition states of an RNA unfolding reaction. Our result shows that time dependent NSET can clearly distinguish structural transitions between unfolded to folded states. Our experimental observation point out that NSET can be used for the design of optical based molecular ruler to track RNA folding transition states at distances more than double the distances achievable using traditional dipole-dipole Columbic energy transfer based methods. Our experimental results point out that RNA folding kinetics becomes slower in the presence of gold nanomaterial, which is due to the strong electrostatic interaction between gold nanomaterial and dye. With very low background signal and high intensity changes during unfolding, NSET will be able to detect intermediates of very low population that are not observable with FRET probes.

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Local Effects of Single Gold Nanoparticles on the Fluorescence Signal of Single Dye Molecules embedded in a Supported Lipid Bilayer revealed by Means of Fluorescence Correlation Spectroscopy

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Since its first introduction in 1972, fluorescence correlation spectroscopy (FCS) has become a versatile and powerful tool for investigating time constants of chemical reactions and biological processes on the single-molecular level. Correlating the temporally fluctuating fluorescence signal of dye molecules that diffuse across the laser focus at very low concentrations (10^{-9} M) allows to determine microscopic parameters such as the diffusion constant D, diffusion time t_D, the average number of molecules in the laser focus <N>, and time constants for photophysical processes.

A basic limitation of FCS is the diffraction-limited resolution of optical microscopy which leads to a minimal observation volume V_{min} of a few femtoliters. Smaller observation volumes would provide access to either an improved spatial resolution of the dynamic process under study, or FCS studies with a much larger dye concentration within the sample. A promising approach for the further downsizing of V_{min} is using spherical gold nanoparticles. Since they exhibit a plasmon resonance in the optical regime, the electromagnetic field may be confined to a very small region in the nanometre range [1].

Here, we discuss the impact of a variety of physical processes, namely the geometry of the bilayer in close proximity to the gold nanoparticle, the quenching of dye molecules close to the nanoparticle surface, as well as anomalous diffusion effects due to force gradients in the curved membrane structure, which have to be taken into account when performing FCS with metallic nanostructures. Moreover, we show that these processes lead to a change in the autocorrelation function of the fluorescence fluctuations originating from the two-dimensional diffusion of dye molecules within the lipid bilayer.

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A biosensor based on localized surface plasmons in noble metal nanoparticles

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Localized surface plasmons (LSPs) are charge density oscillations caused by an interaction of electromagnetic waves with the interface between metallic nanostructures (e.g. noble metal nanoparticles) and a dielectric medium. Excitation of LSPs by an electric field at an incident wavelenght results in strong light scattering, in the appearance of intense surface plasmon (SP) absorption bands. Intensity and frequency of the SP absorption bands are characteristic for the type of material and depends on the size, shape, size distribution and surrounding environments of the nanostructures [1].

We have designed core/shell-nanostructures with a defined Au-core and increasing Ag-shell thickness as described [2]. We used AFM measurement and dark-field microscopy to characterize the nanoparticles, which were immobilized via APTES on borosilicate substrates. The plasmon band of selected particles was investigated by single particle spectroscopy (SPS) in transmission and reflection mode. The spectroscope was coupled by an optical fiber to the microscope where a 50 µm pinhole allows to collect the scattered light of just one chosen metal nanoparticle.

In our work we want demonstrate the potential of designed core/shell-nanoparticles as optical biosensors. For this we treated the nanoparticles with 11-mercaptoundecanoic acid (MUA) to form a biocompatible self-assembled monolayer (SAM) for specific binding of proteins via EDC/NHS standard amine coupling chemistry [3]. The immobilization of the protein and the following incubation with a protein recognizing antibody leads to a refractive index change in the local environment of metal nanoparticles. This causes a characteristic shift of the SP absorption band maximum which was detected spectroscopically as described above.

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SERS Labels for Red Laser Excitation: Silica-Encapsulated SAMs on Tunable Gold/Silver Nanoshells

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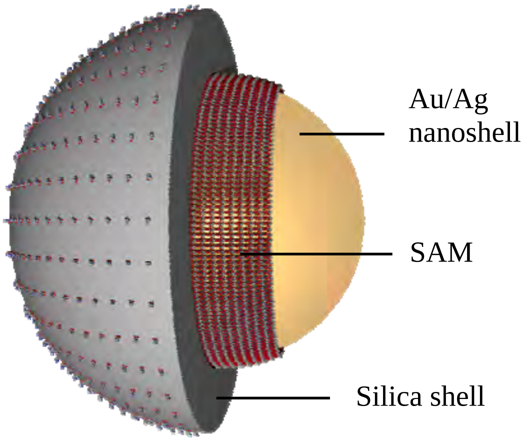
Silica-encapsulated self-assembled monolayers (SAMs) on tunable gold/silver nanoshells for use as surface-enhanced Raman scattering (SERS) labels in bioanalytical and biomedical applications with red laser excitation are presented. This concept combines the spectroscopic advantages of a SAM with the high chemical and mechanical stability of a glass shell. The maximum surface coverage with Raman reporter molecules on the nanoparticles and the uniform molecular orientation leads to a high and reproducible SERS signal. Overall, our improved SERS label design results in ~ 180 times brighter SERS signals compared with existing approaches based on single gold nanospheres. Using SERS-labeled antibodies, the selective localization of prostate-specific antigen (PSA) in the epithelium of prostate tissue specimens by immuno-SERS microscopy with red laser excitation is demonstrated. [1]



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Ultrafast Plasmon Dynamics and Evanescent Field Distribution of Reproducible Surface-Enhanced Raman-Scattering Substrates

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Surface-enhanced Raman scattering (SERS) is a potent tool in bioanalytical science because the technique comprises high sensitivity with molecular specificity. However, a widespread and routine use of SERS in quantitative biomedical diagnostics is limited by tight requirements on the reproducibility of the noble metal substrates used. To solve this problem, some of us recently introduced a novel approach to reproducible SERS substrates. In this contribution we apply ultrafast time-resolved spectroscopy to investigate the photo-induced collective charge-carrier dynamics in such substrates, which represents the fundamental origin of the SERS mechanism. Time-resolved spectroscopy is used to understand the ultrafast charge-carrier dynamics in innovative SERS substrates and pave the way for a systematic study of the SERS enhancement mechanism by nanostructured gold surfaces. The ultrafast experiments are accompanied by scanning-near field optical microscopy and SERS experiments to correlate the appearance of plasmon dynamics with the resultant evanescent field distribution and the analytically relevant SERS enhancement.

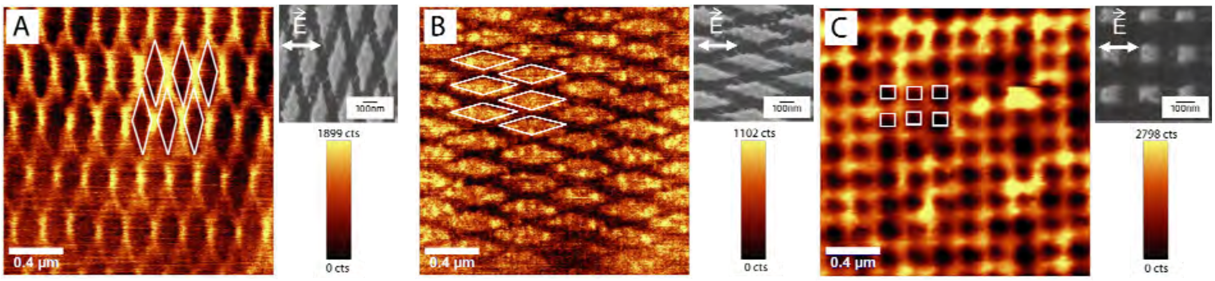

Figure 2. Scanning near-field optical microscopy (SNOM) image of the nanorhombs (A) and (B) and nanosquare (C) surfaces. SNOM experiments in the pick-up mode were performed with laser excitation at 633 nm. Therefore the plasmonic array is illuminated with linear polarized laser light from below and the transmitted light is collected through a small aperture (~150 nm). With the E-field of the incident light being parallel to the short axis of the nanorhombs (A) local field enhancement in the gap between individual nanoparticles is observed. (B) By rotating the plasmonic array by 90 degree, i.e. the E field being parallel to the long axis, only a reduced field enhancement due to the intrinsic roughness of the gold film is detected. (C) SNOM image of the nanosquares.

Synthesis of rod-shaped gold nanorattles with improved plasmon sensitivity and catalytic activity

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We prepared rod-shaped gold nanorattles – solid gold nanorods surrounded by a thin gold shell – using a galvanic replacement process starting with silver-coated gold nanorods. These structures are very promising candidates for catalytic applications and optimized plasmonic sensors. They combine the advantages of rods (low plasmon resonance frequency, large polarizability) with the high surface area of hollow structures. The plasmonic sensitivity Ю = $d\lambda/dn$ to changes in the dielectric environment is up to 50% higher in gold nanorattles compared to gold nanorods with the same resonance frequency and 6x higher than for plasmons in spherical gold nanoparticles. The catalytic activity measured for the reduction of para-nitrophenol is 4x larger than for bare gold nanorods. We discuss the issue what constitutes the optimal plasmonic nanosensors for the detection of changes in dielectric environment.

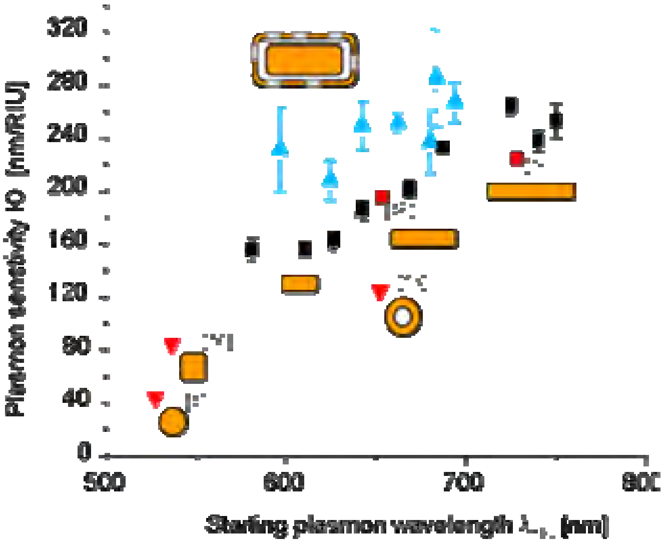

Figure Overview of the sensitivityЮ = $d\lambda_{res}$ / dn of different gold nanostructures: spheres, cubes, rods, shells, and rod-shaped nanorattles. Since the sensitivity depends not only on shape but also on the position of the resonance wavelength, we show the sensitivity values as a function of the plasmon wavelength in water. The values for spheres, cubes, shells, and some rod samples are taken from the literature. Our data for ensemble measurements on different samples of solid gold nanorods (black labels) show lower Ю values than rod-shaped gold nanorattles, produced from these rods (blue labels).

Sensoric potential of (bi)metallic nanoparticles

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During the last decades noble metal nanoparticles have been increasingly applied in the fields of analytics (DNA, food) and diagnostics/therapy (cancer) since they proved as valuable tools in robust and cost efficient devices with possibly optical detection. By the interaction of light with the free electrons in the conduction band of metal nanoparticles a plasmon resonance (LSPR) band is generated caused by collective oscillations [1]. The location of the LSPR band mainly depends on material composition, shape, dimension, and the chemical environment (solvent, ligands) of the nanoparticles [2]. In the talk, sensitivities of core-shell nanoparticles towards changes in the refractive index of the surrounding medium will be shown monitored as the shift of the extinction peak maximum. When compared to sensitivities of nanostructures reported in the literature the (roughly) spherical gold-silver core-shell nanoparticles presented here show higher sensitivities than gold nanorods or silver triangular structures. Further, preliminary results of sensitivity studies will be displayed using nanoparticles on the single nanoparticle level. Single nanoparticle spectroscopy was utilized to detect shifts in the scattering peak prior and after binding of BSA and/or anti-BSA antibodies. Darkfield microscopy and AFM were used in parallel to monitor spectral changes qualitatively and the size of the respective nanoparticle.

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Enzymatically produced silver nanoparticles for manifold areas of bioanalytical applications

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Surface enhanced Raman spectroscopy (SERS) is an emerging technology in the field of analytics. Due to the high sensitivity and specificity through the specific molecular fingerprint information SERS can be used in a variety of analytical, bioanalytical, and biosensing applications. However, for the SERS effect substrates with metal nanostructures are needed. To establish SERS as standard analytical tool substrates, which are easy to produce, inexpensive, reproducible and stable are needed. Nowadays, most SERS substrates are not able to fulfil all of these requirements. Substrates like nanoparticles, which are cheap and easy to produce, are hardly reproducible and need an extensive characterization of their SERS activity prior to their use. In comparison SERS substrates produced by electron beam lithography or nanosphere lithography are highly reproducible but their production is difficult and expensive.

An alternative approach to produce low cost and reproducible substrates for SERS applications, which allows a simple, economical and highly space-resolved production of SERS active surfaces, is based on an enzyme induced deposition of silver nanoparticles. The produced SERS substrate has many advantages. The special structural features of the enzymatically deposited silver nanoparticles allow plasmon absorption in the visible and NIR region, which enables the utilization of different excitation frequencies for SERS and SERRS measurements. Besides a simple and fast characterization of the SERS enhancement is possible. These properties make SERS substrates of enzymatically deposited silver appropriable for multiple analytical interrogations.

Acknowledgement

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High-Resolution Surface Plasmon Imaging

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Electron energy loss spectroscopy (EELS) in combination with scanning transmission electron microscopy (STEM) is emerging as a novel characterization tool in plasmonics [1]. The high spatial resolution of electron-based microscopy together with the improved energy resolution in the sub-eV range render EELS ideal for the study of plasmonic structures, with possible applications for optical data processing, negative refraction, or biosensors, which have seen tremendous interest in recent years.

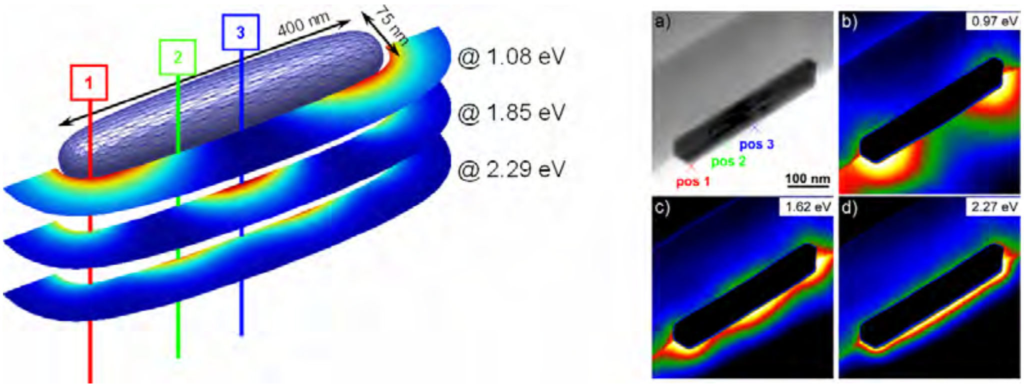

Figure 1: Results of a boundary element method simulation (left panel) and experiment (right panel). Triangulated surface of rod-shaped nanoparticle and EFTEM maps as computed and measured according to the prescription of Ref. [2].

In this talk I discuss the theoretical fundamentals of EELS and EFTEM and show results for gold nanoparticles, obtained by experiment and simulation [2].

When an electron beam with kinetic energy in the hundred keV range passes by or through a nanoparticle, the electrons can excite surface plasmons and lose energy, which is subsequently monitored. We calculate the dielectric response of the nanoparticle within the boundary element method (BEM) framework by means of auxiliary surface charges and currents, which allow us to compute for a given frequency the induced electric field at the positions of the electron beam and to express the energy-loss probabilities [3]. We encounter a process reminiscent of a self-energy, where the electron beam induces charge oscillations on the metallic nanoparticle, which produce an electromagnetic field that acts back on the electron beam. The induced potential can be computed by means of the electrostatic Green function.

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Nanometric apertures to enhance single molecule fluorescence detection

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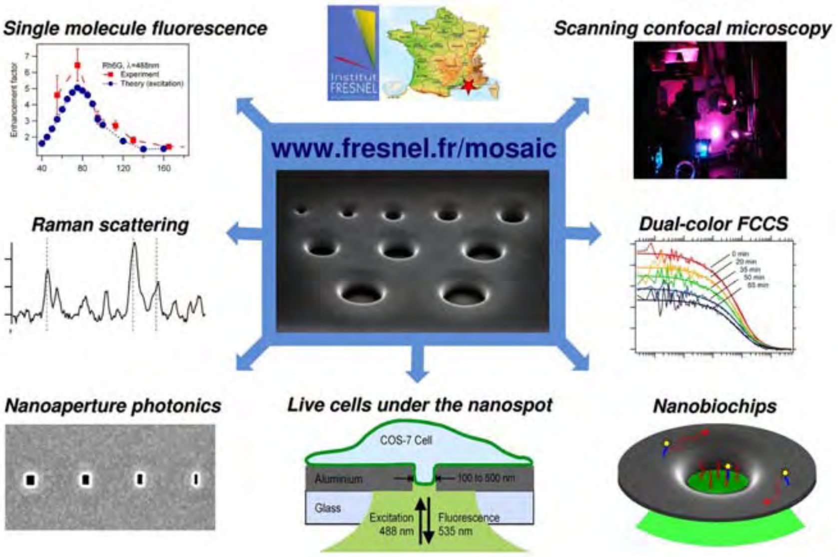
Milling nanometric apertures in a metallic film is an intuitive way to manufacture new nanophotonic devices that are robust and highly reproducible. Although the concept appears very simple, such apertures exhibit attractive properties for biophotonics, such as localization of excitation light, strong isolation from emission produced by species located outside the aperture, and an increase in the fluorescence signal [1]. The simplicity of the structures and their ease of use should further expand their application towards the real-time detection and identification of a low number of molecules.

In this contribution, we review the assets of single nanometric apertures combined with fluorescence correlation spectroscopy (FCS) for single molecule fluorescence analysis. Single subwavelength apertures milled in a metallic film can be used to enhance the fluorescence emission of single molecules, with an enhancement factor up to 12 as compared to the emission rate per molecule in open solution for an optimised design [2-4].

The nanoapertures also allow an observation volume that is smaller than the diffraction limit in optics, enabling efficient enzymatic reactions monitoring at micromolar concentrations for FCS or FCCS [1,5,6]. Moreover, the optimised fluorescence enhancement offers a gain in signal to noise ratio of about one order of magnitude, corresponding to a 100-fold reduction of the FCS experiment duration [6]. This evidences the feasibility of FCS analysis with fast integration times of about one second, opening the way to the monitoring biochemical reactions at reduced time scales. Last, these nanostructures can also be used to investigate the lateral diffusion of lipids and chimeric proteins into live cell membranes [7].



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Single-molecule fluorescence in gold nanoapertures: detailing the role of excitation and emission enhancements

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Subwavelength apertures milled in a metallic film can significantly enhance the fluorescence emission rate of molecules diffusing inside of them [1]. This phenomenon stems from the electromagnetic enhancement of the excitation field inside the aperture, and also from modifications of the emission properties of the emitter (quantum efficiency and emission diagram). Understanding the relative weight of these effects in the total fluorescence signal is a crucial knowledge to design nanostructures for high-efficiency single-molecule analysis.

In this communication we present a comprehensive study of the fluorescence emission of dyes freely diffusing inside circular apertures milled in a 200 nm thick gold film with diameters from 80 up to 350 nm [2]. Fluorescence correlation spectroscopy (FCS) experiments (Fig. 1) allow a quantitative estimation of the fluorescence emission enhancement factor at the single-molecule scale. Moreover, we present an experimental method to discriminate the excitation and emission contributions to the enhancement factor [3]. A broad range of aperture diameters is characterized. The results are discussed in light of electromagnetic numerical simulations.

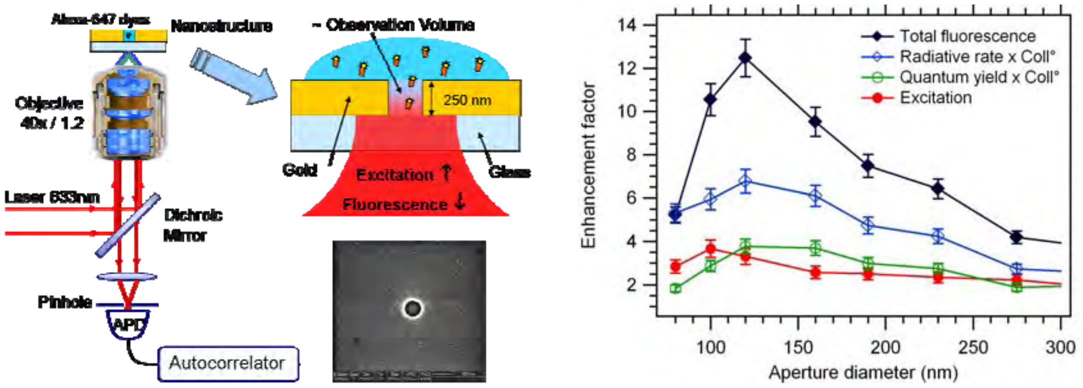

Fig. 1: (Left) Schematic view of the experimental setup: the emission from dyes diffusing in a nanoaperture is detected through a confocal microscope in epi-fluorescence configuration. (Right) Physical contributions to nanoaperture enhanced fluorescence, plotted versus the aperture diameter and normalized to the open solution case.

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Molecular and Biomolecular Sensing with Nanoparticles

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Three different effects of the localized plasmon of Au nanoparticles (NPs) were implemented for the development of molecular and biomolecular sensing platforms:

(i) The plasmon absorbance of Au NPs was used to develop enzyme-based sensors for glucose or ethanol. The biocatalytic growth of the Au NPs was controlled by the concentration of the respective substrates, and this enabled the optical sensing of the substrates.

(ii) The aggregation of Au NPs leads to interparticle plasmon coupling, and to the formation of a red-shifted plasmonic exciton. This effect was used to sense Hg^{2+} by T-rich nucleic acid-functionalized Au NPs.

(iii) The coupling of the localized plasmon of Au NPs with the surface plasmon wave associated with Au NPs results in a significant shift in the surface plasmon resonance. Accordingly, Au NPs were used as amplifying units for recognition events on Au surfaces: (a) Au NPs composites crosslinked to π-donor bis-aniline bridging units were linked to Au surfaces. The resulting composites were used for the ultra-sensitive surface plasmon (SPR) analysis of the explosives TNT or RDX. Methods to imprint the composites for the specific analytes will be described, and a theoretical description addressing the origin for the high sensing sensitivity will be presented.

Other, aptamer-based, biosensors based on the coupling of the localized Au NPs labels with Au films will be presented.

Finally, the plasmonic effects of semiconductor nanoparticles (quantum dots, QDs) were used for the multiplexed analysis of ions, and for the development of logic gate operations. This will be exemplified with the use of two, differently sized, CdSe/ZnS QDs that were functionalized with T-rich or C-rich nucleic acids. The multiplexed analysis of Hg^{2+} and Ag^{+} by the QDs was achieved by following the fluorescence quenching of the QDs by the ions. Also, in the presence of Hg^{2+} and Ag^{+} as inputs the "OR" or "AND" logic gates were designed.

Link pH indicator molecules to gold nanoparticles

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In cell biology, pH has a great importance as changes in its concentration are involved in many enzymatic reactions and metabolic processes. Nano-sensor based on nanoparticles is believed to be promising for detecting the intracellular pH. NHS-SNARF as a popular pH indicator molecule, showed well pH sensitivity at near neutral pH range after it linked with diamine PEG (poly ethylene glycol). The reaction products amine-PEG-SNARF can be separated and extracted by gel electrophoresis. Amphiphilc polymer coated gold nanoparticles were used to conjugate with NHS-SNARF. However, with high density of carboxylic group, after conjugate with NHS-SNARF by using diamine PEG molecules of different lengths, the pH sensitivity tests showed the longer the lengths of diamine PEG molecules decrease, the more of SNARF molecules' pKa shifted to the basic pH range. This pKa shift of SNARF molecule was speculated that the high density of negatively charged carboxylic groups on the surface of polymer coated gold nanoparticles, which attracted many protons and made the pH of local environment near particle surfaces much lower than the bulk solution. To verify this hypothesis, several control experiments with designed surface properties of gold nanoparticles were synthesized and the results of the pH tests after linked with NHS-SNARF were compared with one another and discussed in details.

Directed Growth of Metallic Nanoparticles on DNA Templates

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We report on the synthesis and growth characterization of silver nanoparticles on chemically modified DNA templates in aqueous-phase. A classical method, involving the controlled nucleation and growth of silver nanoparticles from silver nitrate and sodium citrate, was used to provide the necessary chemistry. By keeping this solution at a slow reaction condition, nanoparticle nucleation could be selectively achieved at DNA label sites. This was accomplished by irradiation of photoactive cyanine dye molecules attached to the DNA. Systematic studies on solution concentrations, irradiation times, and temperatures by extinction spectroscopy and dynamic light scattering (DLS) provided the optimal conditions for the process and also insight of the roles of the components, e.g.,: In the classical method sodium citrate is used as a reducing agent. In contrast, the presence of sodium citrate in the suggested method both slows the particle growth and promotes a smaller particle size distribution of 5 to 40 nm with a peak at a. 10 nm, this was also independently confirmed by transmission electron microscopy (TEM). This stabilization of the solution is comparable to the influence of a capping agent in similar systems. The occurrence of a plasmon peak in the extinction spectra verifies the metallic structure of the particles. The separation via centrifugation of the DNA molecules and obtained particles confirmed the silver particles are attached to DNA molecules, i.e., that DNA-silver-particle conjugates were formed. These structures can be used for the energy transfer measurements between fluorescent dyes and a silver nanoparticle. The DNA-silver-particle conjugates can be tailored with respect to DNA length, particle size and predesigned end groups and thus hold the potential to form novel 3 dimensional structures for, e.g., nanophotonics.