

ABSTRACTS

MOLECULAR PLASMONICS 2017

MAY 18 – MAY 20, 2017

Leibniz-IPHT // Campus Beutenberg // Jena

www.leibniz-ipht.de

sponsored by



Leibniz
Leibniz
Association

TALKS

- 3 | **Strong Biexciton Emission Enhancement of a Single Quantum Dot by a Plasmonic Nanocone Antenna** // Vahid Sandoghdar
- 4 | **Templated assembly of plasmonic nanoparticles** // Luis M. Liz-Marzán
- 5 | **Dynamics of strongly coupled modes between surface plasmon polaritons and photoactive molecules: the effect of the Stokes shift** // Jussi Toppari
- 6 | **High Temperature Photonics** // Manfred Eich
- 7 | **Plasmonic biosensors and their bioanalytical applications** // Jirí Homola
- 8 | **Novel bioanalytical perspectives of plasmonic interfaces** // Mihaela Gheorghiu
- 9 | **Plasmonic and Luminescent Nanoprobes for *in vivo* Cell Imaging** // Oihane Fragueiro
- 10 | **Nanodiagnostics for Detection of Tuberculosis** // Hassan M. E. Azzazy
- 11 | **Plasmonic-heating-induced nanofabrication using gold nanoparticles** // Shuichi Hashimoto
- 12 | **Overcoming photo-thermal effects for the fabrication of dimers with sub-diffraction gaps by optical printing** // Thomas Brick
- 13 | **Nanogap-Enhanced Raman Scattering (NERS)** // Yung Doug Suh
- 14 | **Surface-enhanced Raman spectroscopy as tool for bioanalytical and biomedical detection schemes** // Dana Ciiala-May
- 15 | **Combination of surface enhanced Raman and hyper-Raman imaging using hyperspectral analysis** // Zsuzsanna Heiner
- 16 | **The behaviour of molecular-plasmonic assemblies in solution** // Martin Werts
- 17 | **Gold Nanoparticles enable Charge Transfer across Phospholipid Bilayer Membranes** // Mathias Brust
- 18 | **Thermal and electron induced damage to DNA on laser illuminated plasmonic nanoparticles** // Robin Schürmann
- 19 | **Gold Nanorod-Enhanced Fluorescence Enables Single-Molecule Electrochemistry of Methylene Blue** // Weichun Zhang
- 20 | **Confining Brownian motion of nanoparticles and biomolecules in an ABELtrap** // Maria Dienerowitz
- 21 | **Plasmon Rulers for the Unraveling of Single-Molecule Polyethylene Glycol Dynamics** // Weixiang Ye
- 22 | **Probing of biomolecular films and their temperature-induced transitions with rotating gold nanorods** // Hana Šípová

STRONG BIEXCITON EMISSION ENHANCEMENT OF A SINGLE QUANTUM DOT BY A PLASMONIC NANOCONE ANTENNA

Vahid Sandoghdar // Max Planck Institute for the Science of Light, Erlangen, Germany

Semiconductor quantum dots are useful emitters in various contexts. They are, for example, a bright source of photons because of the possibility to generate multiple excitons within one quantum dot and subsequently obtain the emission of multiple photons upon each excitation. In practice, however, such multiphoton emission is often inefficient due to fast nonradiative decay channels such as Auger recombination. We have recently demonstrated that the biexciton emission efficiency can be significantly improved by a large radiative enhancement in the near field of a gold nanocone antenna [1].

Our experimental configuration is shown in Fig. 1a. Using shear-force control, a single quantum dot attached to the end of a glass tip is approached to a glass surface, carrying gold nanocone antennas fabricated by focused ion beam milling [2]. This configuration allows us to position a single quantum dot with respect to a gold nanocone with nanometer accuracy. The normalized decay rates measured at various quantum dot-nanocone lateral displacements nicely demonstrates the strong distance dependence in Fig. 1b. The figure also shows that the second-order autocorrelation function at zero time delay ($g^{(2)}(0)$) becomes larger at smaller displacements, pointing to the enhancement of the biexciton emission in the vicinity of the nanocone antenna.

In order to gain a deeper insight into the observed enhancement, we measured the saturated emission rate at the smallest displacement using a pulsed laser at low repetition rate. This additional measurement allowed us to record the increase of the quantum efficiencies of the monoexciton and biexciton emissions from 22 % and 6.5 % to 60 % and 71 %, respectively, in the near field of the nanocone antenna. In other words, we find that a plasmonic nanocone has enhanced the biexciton emission efficiency by more than one order of magnitude. Furthermore, we discuss how the knowledge of the quantum efficiency enables us to decompose the total decay rate into its radiative and nonradiative contributions. We show that the nanocone antenna enhances the radiative decay rate by about 110 for the monoexciton emission and 100 for the biexciton emission. Future improvements should allow for enhancement factors in range of several thousands [3].

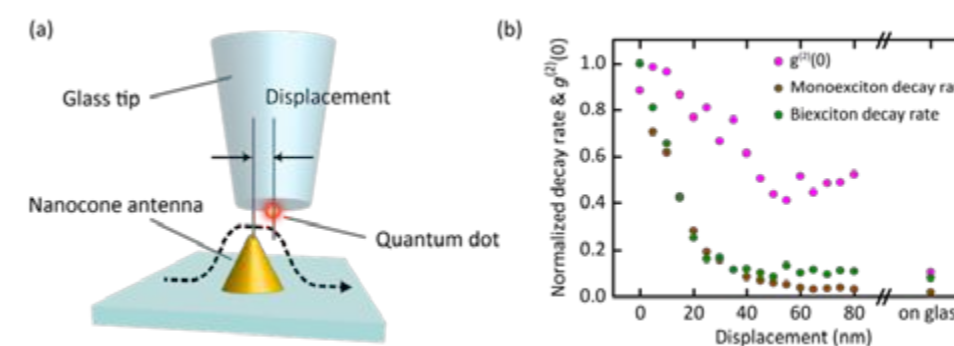


Fig. 1 (a) Schematic of the experiment. (b) Normalized decay rates of monoexciton (brown) and biexciton (green) emission as a function of the displacement between the quantum dot and the nanocone. The $g^{(2)}(0)$ measured at each displacement is also plotted (pink).

References:

- [1] K. Matsuzaki, S. Vassant, H.-W. Liu, A. Dutschke, B. Hoffmann, X.-W. Chen, S. Christiansen, M. R. Buck, J. A. Hollingsworth, S. Götzinger, and V. Sandoghdar, "Scientific Reports, 7, 42307 (2017).
- [2] B. Hoffmann, S. Vassant, X.-W. Chen, S. Götzinger, V. Sandoghdar, and S. Christiansen, Nanotechnology 26, 404001 (2015).
- [3] X. Chen, M. Agio, V. Sandoghdar, Phys. Rev. Lett. 108, 233001 (2012).

Luis M. Liz-Marzán // CIC biomaGUNE, Paseo de Miramón 182, 20014 Donostia-San Sebastián, Spain, Ikerbasque, Basque Foundation for Science, 48013 Bilbao, Spain

The integration of nanoparticle superstructures into daily life applications faces major challenges including the simplification of the self-assembly process, reduced cost and scalability. It is however often difficult to improve on one aspect without losing on another. Stamping and templated assembly have been used to create single- and multi-particle patterns, but these are typically limited to a small number of particles. We have recently developed a bench-top method that allows patterning a macroscopic substrate with gold nanoparticle supercrystals in a one-step process [1]. The method allows parallelization and patterned substrates can be made with high throughput. The self-assembly of a variety of building blocks into crystalline superstructures takes place upon solvent evaporation and their precise placement over millimeter scale areas is induced by confinement of the colloidal suspension in micron sized cavities. We mainly focus on gold nanorods and demonstrate their hierarchical organization up to the device scale. The height of the formed nanorod supercrystals can be tuned by simply varying nanorod concentration, so that the topography of the substrate and the resulting optical properties can be readily modulated [2]. Additionally, the use of templates with different morphologies can be replicated into assemblies with tailored shape and size [3].

Funding by the European Research Council (ERC Advanced Grant Plasmaquo) is gratefully acknowledged.

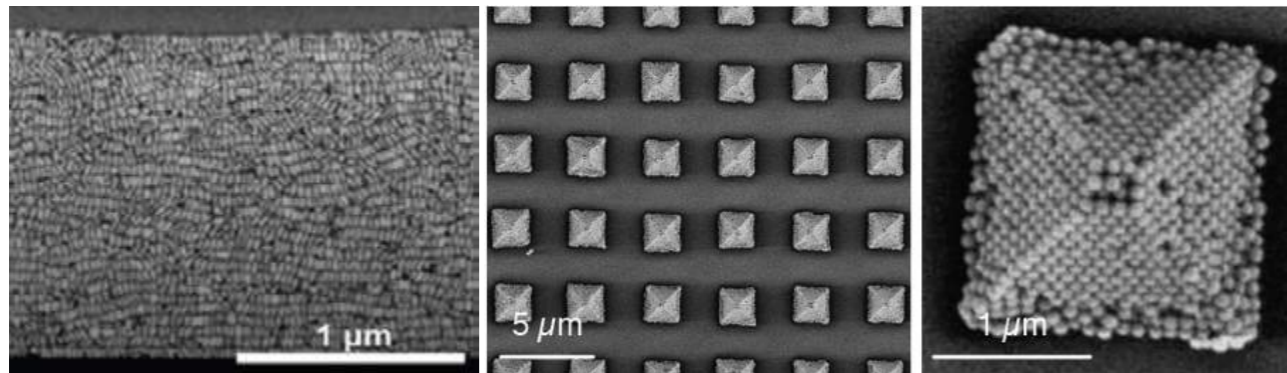


Fig. 1: SEM image of the cross-section of a gold nanorod supercrystal, Fig. 2: SEM images of pyramidal gold nanosphere supercrystals at different magnifications.

References:

- [1] C. Hamon, S. Novikov, L. Scarabelli, L. Basabe-Desmonts, L.M. Liz-Marzán, ACS Nano 8 (2014), 10694-10703.
- [2] C. Hamon, M.N. Sanz-Ortiz, E. Modin, E.H. Hill, L. Scarabelli, A. Chuvilin, L.M. Liz-Marzán, Nanoscale 8 (2016), 7914-7922.
- [3] G. Bodelón et al., Nature Mater., in press. DOI: 10.1038/NMAT4720. Plasmonic biosensors and their bioanalytical applications 0533–10539.

Svitlana Baieva, Ossi Hakamaa, Gerrit Groenhof¹, Tero Heikkilä, Jussi Toppari // University of Jyväskylä, Department of Physics and ¹Department of chemistry, Nanoscience Center, P.O. Box 35, 40014 University of Jyväskylä, Finland

Already for some time the coupling between surface plasmon polaritons (SPP) and molecules has been utilized in plasmonics. In addition to regular absorption and emission, the regime of strong coupling has been demonstrated for a variety of molecules and plasmonic systems [1]. This strong coupling manifests itself by the appearance of an avoided crossing, i.e. Rabi splitting, in the SPP dispersion at the point of the molecule absorption, due to formation of new hybrid polariton states.

We have investigated the dynamics of these polariton states by analyzing their scattered emission [2]. While the scattered emission of SPP is purely transverse magnetic (TM) polarized, the strong coupling with molecules induces transverse electric (TE) component to the emission via the partial molecular nature of the hybrid state. We observe that the TM/TE ratio of the polariton emission follows the contribution of the molecular states in this hybrid mode, which is determined by the coupling strength. In addition, the Stokes shift of the molecule fluorescence seems to influence the polarization of the emission - the larger the shift the lower the TE polarized emission.

We argue that due to random orientation of the molecules, the emission of a fully coherent SPP-molecule polariton should be purely TM-polarized, like SPP. However, as result of the unique micro-environments of the molecules in combination with thermal motion, this symmetry may break for individual excitations, providing a route to the TE emission. The experimental results agree qualitatively with this model including the symmetry breaking as shown in Figure 1. Furthermore, the relaxation rate of the polariton correlates with the Stokes shift, so that TE emission can only occur if the Stokes shift is small and consequently the lifetime is long enough. Theoretical models that include microscopic details of the molecules will be essential to systematically exploit strong coupling for plasmonics or even controlling chemical reactions.

Funding by Academy of Finland is gratefully acknowledged.

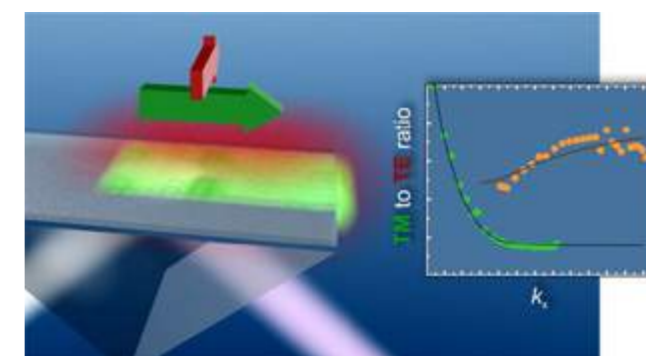


Fig. 1. Schematics of the experiments on the strongly coupled polariton modes between SPPs and molecules. The measurements are carried out via prism coupling in Kretschmann geometry and arrows point the polarizations of interest. Inset shows the measured polarization ratio as a function of the wave vector, k_x , together with a fit by the developed theory.

References:

- [1] P. Törmä, P. and W. L. Barnes, Rep. Prog. Phys. 78 (2015) 013901.
- [2] S. Baieva, O. Hakamaa, G. Groenhof, T.T. Heikkilä, J.J. Toppari, ACS Photonics 4 (2017) 28.

Manfred Eich^{1,4}, **Alexander Yu. Petrov**^{1,2}, **Pavel N. Dyachenko**¹, **Sean Molesky**³, **Slawa Lang**¹, **G. Shang**¹, **Michael Störmer**⁴, **T. Krekeler**⁵, **M. Ritter**⁵, **Jacob Zubin**^{3,6}, **G. Schneider**⁷, **J. do Rosario**⁷ // ¹Institute of Optical and Electronic Materials, Hamburg University of Technology (TUHH), Eißendorfer Straße 38, 21073 Hamburg, Germany / ²ITMO University, 49 Kronverskii Ave., 197101, St. Petersburg, Russia / ³University of Alberta, Department of Electrical and Computer Engineering, 9107-116 Street, T6G 2V4, Edmonton, Canada / ⁴Institute of Materials Research, Helmholtz-Zentrum Geesthacht, Max-Planck-Straße 1, 21502 Geesthacht, Germany / ⁵Electron Microscopy Unit, TUHH, Eissendorfer Strasse 42, 21073 Hamburg, Germany / ⁶Birck Nanotechnology Center, School of Electrical and Computer Engineering, Purdue University, West Lafayette, IN 47906, USA / ⁷Institute of Advanced Ceramics, Hamburg University of Technology (TUHH), Denickestraße 15, 21073 Hamburg, Germany

Recent research results will be presented on selective emitters and near field radiative transfer for thermophotovoltaics and on tailored mid infrared radiation reflectors for novel thermal barrier coatings. Emission of thermal radiation is a fundamental physical process defined by the dielectric properties of the thermally excited materials. Radiation into far field is described by Planck's law and is limited by the blackbody emission. In near field additional thermal energy transfer can be achieved due to evanescent fields, which are orders of magnitude larger than in far field. Here we present multiscaled nanostructured materials to enhance the thermal transport in near field and provide selective emission in far field. We demonstrate selective band edge emitters for thermophotovoltaics stable up to 1000 °C based on W-HfO₂ refractory plasmonic metamaterials and ZrO₂ based ceramic resonators on metallic tungsten.

We demonstrate coatings with high reflectivity in the wavelength range of 1-6 µm and low thermal conductivity at the same time. These coatings show a thermal stability up to 1400 °C and thus are a prime candidate for novel reflective thermal barrier coating used on aircraft turbine blades.

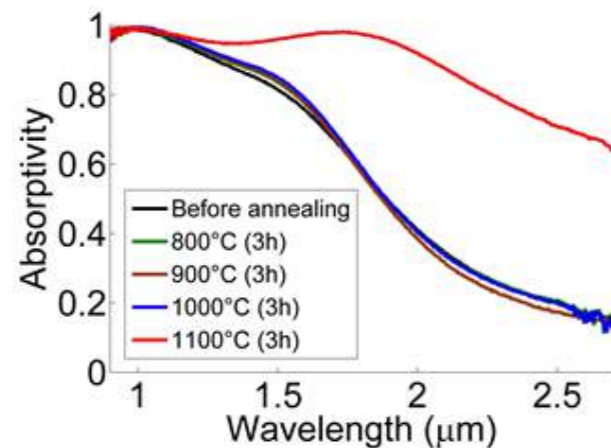


Figure 1. a) Absorptivity of the tungsten based metamaterial after annealing in vacuum. Schematic inset shows the layered structure of the W-HfO₂ (20 nm-100 nm) plasmonic metamaterial. We further report on high-temperature stable ceramic photonic structures which benefit from a tailored reflectivity and the high temperature stability inherent to refractory ceramics.

References:

- [1] P.N. Dyachenko, S. Molesky, A. Yu Petrov, M. Störmer, T. Krekeler, S. Lang, M. Ritter, Z. Jacob, and M. Eich, Nat. Commun. 7, 11809 (2016)
- [2] E.W. Leib, R.M. Pasquarelli, J.J.do Rosario, P.N. Dyachenko, S. Doring, A. Puchert, A.Y. Petrov, M. Eich, G. Schneider, R. Janssen, H. Weller, T. Vossmeier, Journal of Materials Chemistry C, vol. 4, no. 1, pp. 62–74 (2016)
- [3] S.-A. Biehs, S. Lang, A.Y. Petrov, M. Eich, P. Ben-Abdallah, Physical Review Letters, vol. 115, no. 17, p. 174301–174301, (2015)
- [4] P.N. Dyachenko, J.J. do Rosário, E.W. Leib, A.Y. Petrov, M. Störmer, H. Weller, T. Vossmeier, G. Schneider, M. Eich, Optics Express, vol. 23, no. 19, pp. A1236 (2015)
- [5] P.N. Dyachenko, J.J. do Rosário, E.W. Leib, A.Y. Petrov, R. Kubrin, G. Schneider, H. Weller, T. Vossmeier, M. Eich, ACS Photonics, vol. 1, no. 11, pp. 1127–1133 (2014)

Jiří Homola // Institute of Photonics and Electronics, Czech Academy of Sciences, Chaberská 57, 18251 Prague, Czech Republic

This paper presents selected results of research into plasmonic biosensors at the Institute of Photonics and Electronics, Prague. Research into plasmonic biosensors is truly multidisciplinary research [1], and therefore the reported results span across several disciplines. Advances in the preparation of plasmonic nanostructures using the top-down nanofabrication methods, such as the multiple-beam interference lithography [2], will be presented. Trends in optical instrumentation for plasmonic biosensors, including multiplexed optical platforms for massively parallelized detection and compact optical platforms for the detection of chemical and biological analytes in the field, will be discussed. Transport of target molecules in microfluidic systems of plasmonic biosensors and effects of transport on performance of plasmonic biosensors will be also covered [3]. In addition, attention will be given to functional coatings for plasmonic (nano)structures, in particular to new functional coatings based on polymer brushes with ultra-high resistance to fouling from complex biological media [4]. Advanced methodologies for the detection of extremely low levels of molecular analytes in biological samples (e.g. referencing and amplification strategies) will be also discussed. Moreover, examples of applications of plasmonic biosensors for the detection of nucleic acid and protein biomarkers and foodborne pathogens (Fig. 1) will be given.

This research was supported by the Czech Science Foundation (contract # GBP205/12/G118) and by Praemium Academiae of the Czech Academy of Sciences.

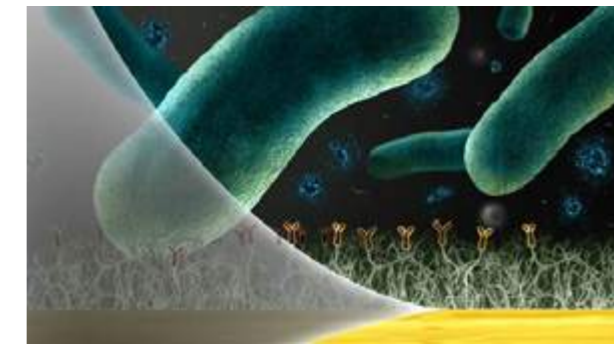


Fig. 1: Detection of foodborne bacterial pathogens using a plasmonic biosensor functionalized by a carboxy-functional zwitterionic polymer brush.

References:

- [1] B. Špacková, et al., Proceedings of the IEEE, 104 (2016) 2380–2408.
- [2] M. Vala and J. Homola, Optics Express, 24 (2016) 15656–15665.
- [3] N. S. Lynn Jr. and J. Homola, Analytical Chemistry, 88 (2016) 12145–12151.
- [4] H. Vaisocherová-Lísalová, et al., Analytical Chemistry, 88 (2016) 10533–10539.

Mihaela Gheorghiu, Sorin David, Alina Vasilescu, Cristina Polonschii, Szilveszter Gaspar, Eugen Gheorghiu
// International Centre of Biodynamics, 1B Intrarea Portocalelor, 060101 Bucharest 6, Romania

The exquisite analytic potential of plasmonic nano-interfaces matured into powerful approaches able to shed a new perspective on bioaffinity interactions and on cellular organization.

We advance solutions to surpass current limitations of plasmonic based sensing assays via innovative chip structure, tailored measurement, and improved methods for data analysis.

Selected case studies involving Magneto Optical Surface Plasmon Resonance (MOSPR) 1, plasmonic based Electrochemical Impedance Spectroscopy, EIS2 assays will be presented. P-EIS combines EIS and Surface Plasmon Resonance, SPR, capabilities by deploying an electrode exhibiting plasmonic properties in a set-up combining an AC signal generator (as the ones used for EIS) and a SPR module.

P-EIS outstanding applicative potential that spans from biosensing to analysis of living cells will be outlined in the context of novel plasmonic EIS systems currently developed within ICB.

Recent applications involving versatile SPR detection of lysozyme³ as well as label free platforms for detection of amyloid fibrils effect on live cells⁴ will be as well highlighted.

Acknowledgement:

Support through Romanian National Contracts No. 11/2012, ID: PN II-ID-PCCE-2011-2-0075 and PN-III-P2-2.1-PED-2016-1137.

References:

- [1] S. David et al., *Biosensors & Bioelectronics* 2015, 63, 525-32.
- [2] C. Polonschii et al., *Analytical Chemistry* 2014, 86 (17), 8553-62.
- [3] [a] A. Vasilescu et al., *Biosensors & Bioelectronics* 2016, 83, 353-60; [b] A. Vasilescu et al., *Biosensors & Bioelectronics* 2017, 89, 525-531.
- [4] M. Gheorghiu et al., *Biosensors & Bioelectronics* 2014, 52, 89-97. Plasmonic and Luminescent Nanoprobes for in vivo Cell Imaging

Oihane Fragueiro¹, Joan Comenge², Dom Belic¹, Jack Sharkey³, Marcin Grzelczak¹, Raphael Lévy², Mathias Brust¹ // ¹Department of Chemistry, University of Liverpool, L69 7ZD, UK, ²Institute of Integrative Biology, University of Liverpool, L69 7ZB, UK, ³Institute of Translational medicine, University of Liverpool, L69 3BX, UK

Gold Nanorods (GNRs) are excellent contrast agents for in vivo imaging and photothermal therapies due to their optical properties¹. Their Longitudinal Surface Plasmon Resonance (LSPR) can be tuned and shifted to the Near Infrared (NIR) where endogenous absorbance of biological tissue is minimal. This region of the spectrum is called the therapeutic or NIR window. The heat conversion of the light absorbed by the LSPR, ultimately leads to an ultrasound wave which can be recorded by Multispectral Optoacoustic Tomography (MSOT). MSOT is a novel non-invasive imaging method derived from photoacoustic imaging (PAI). Its good spatial and temporal resolution and high sensitivity make MSOT an exceptional technique for preclinical imaging. GNRs were synthesised by the seeded growth method², and modified via ligand exchange using a small thiolated PEG with a carboxylic acid group. One million mesenchymal stem/stromal cells (MSCs) have been visualised for up to 19 days after subcutaneous injection in mice (Figure 1). However, lungs and bone cannot be imaged with this technique. For this purpose, persistent luminescent nanoparticles could be used as promising in vivo probes³. Their emission lifetime is in the order of minutes. This allows imaging of the whole animal avoiding excitation during the measurement, reducing the auto-fluorescence of tissue and therefore improving the signal to noise ratio. By combining both probes, a bimodal imaging approach can be achieved.

Funding by the ERC Advanced Grand, project 321172 PANDORA and the Regenerative Medicine Platform (UKRMP) are gratefully acknowledged.

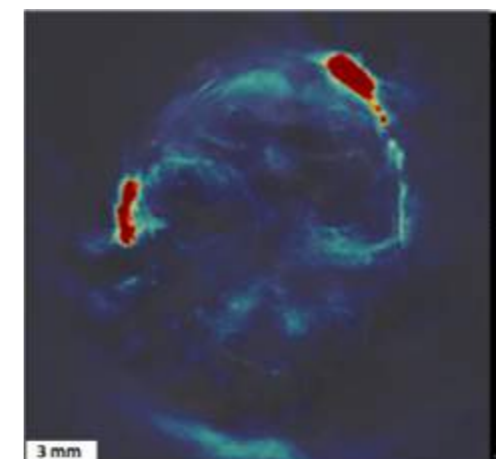


Fig. 1: Cross-section of a mouse showing 2 regions where GNRs-labelled cells were injected (red regions).

References:

- [1] J. Comenge, O. Fragueiro, J. Sharkey, A. Taylor, M. Held, N. C. Burton, B. K. Park, B. Wilm, P. Murray, M. Brust and R. Lévy, *ACS Nano*, 2016, 10, 7106–7116.
- [2] B. Nikoobakht and M. A. El-Sayed, *Chemistry of Materials*, 2003, 15, 1957–1962.
- [3] Z. Li, Y. Zhang, X. Wu, L. Huang, D. Li, W. Fan and G. Han, *Journal of the American Chemical Society*, 2015, 137, 5304–5307.

Hassan M. E. Azzazy, PhD, DABCC, FACB // Novel Diagnostics & Therapeutics Research Group, Department of Chemistry, School of Sciences & Engineering, The American University in Cairo, New Cairo, Egypt 11835

hazzazy@aucegypt.edu

Each year, Mycobacterium tuberculosis (MTB) kills ~one million individuals and infects several millions worldwide. End TB strategy aims at ending the tuberculosis epidemic by 2030. A cornerstone of this strategy is the development of accurate, rapid, and affordable MTB diagnostics. Although several innovative strategies for detection of MTB have been introduced over the past decade, none meets the critical clinical demands for ending the epidemic and, therefore, conventional methods remain necessary for diagnosis especially in heavy burden areas where MTB is most spread.

Unique optical and physical properties of nanoparticles have enabled their utilization for detection of biomarkers of infectious agents. Currently, around thirty-five nanoassays have been developed and partially or fully characterized for detection of MTB using DNA, immunological, or metabolite-based approaches [1]. Accuracy, low cost, and short turnaround time represent the main criteria of the introduced platforms. TB nanodiagnostics encompass several clinical manifestations of the disease including active TB, non-tuberculous mycobacteria, resistant TB, latent TB, and extra-pulmonary TB.

We have previously developed a colorimetric nanoassay prototype for detection of MTB 16s rDNA amplified by PCR using genus- and species-specific oligotargeters and spherical AuNPs (14 nm) [2]. In a second prototype, MTBC unamplified genomic DNA was directly detected using species-specific oligotargeters and AuNPs. Detection limits were 1 ng for PCR product and 40 ng for genomic DNA. The colorimetric nano-gold prototype showed 100% concordance with automated liquid culture system and semi-nested PCR. In a second study, cationic AuNPs were used for sensitive detection of MTB IS6110 gene amplified using conventional PCR. Spherical chitosan coated cationic AuNPs were synthesized and used to detect IS6110 amplicons based on charge interactions. The nano-gold assay was able to colorimetrically detect MTB with a turnaround time of about 1h and a detection limit of 5.4 ng of DNA [3]. The use of AuNP for detection of IS110 amplicons can circumvent gel-based detection of amplicon and reduce contamination risk. Running the assay using an open source PCR thermal cycler would allow a low cost option for molecular detection of MTB. In a third study, we have developed AuNP based FRET assay to detect unamplified MTB DNA extracted from 72 Mycobacterium samples (confirmed by multiplex PCR and 16S-23S ITS sequencing). The assay successfully identified MTB 16s rDNA with sensitivity, specificity, and detection limit of 98 %, 90 %, and 10 ng / μ L; respectively [4]. TB nanodiagnostics have the potential to meet the demand for accurate and affordable TB tests and support ending the global TB epidemic.

References:

- [1] El-Samadony H, Althani A, Tageldin MA, Azzazy HM. Nanodiagnostics for tuberculosis detection. *Expert Rev Mol Diagn.* 2017 Mar 20. doi: 10.1080/14737159.2017.1308825
- [2] Hussain, M.M., Samir, T.M., Azzazy, H.M.E. Unmodified gold nanoparticles for direct and rapid detection of Mycobacterium tuberculosis complex. *Clin Biochem.* 2013; 46(7-8):633-7.
- [3] Tammam SN, Khalil MA, Abdul Gawad E, Althani A, Zaghoul H, Azzazy HM. Chitosan gold nanoparticles for detection of amplified nucleic acids isolated from sputum. *Carbohydr Polym.* 2017 May 15;164:57-63.
- [4] Mansour A, Tammam S, Althani A, Azzazy HME. A single tube system for the detection of Mycobacterium tuberculosis DNA using gold nanoparticles based FRET assay. Submitted to *Journal of Microbiological Methods.*

Yuki Osaka, Issei Aibara, Shinya Mukai, Shuichi Hashimoto // University of Tokushima, 2-1 Minami-josanjima, 770-8506 Tokushima, Japan

Plasmonic heating effect on photoexcitation of gold nanoparticles (NPs) and nanostructures (NSs) finds wide application to various fields: drug delivery, cancer therapy and vapor bubble generation.¹ Here we show our attempts to nanoscale fabrication and structuring. First, we describe nanohole fabrication on glass substrates.² Au nanospheres supported on borosilicate or quartz glass substrate were illuminated with a focused laser beam with a wavelength of 488 nm, which excited both the interband and the localized surface plasmon resonance (LSPR) band of Au NP (Fig. 1). We observed immediate embedding of Au NPs, which was monitored in situ with the white light scattering spectral red-shifts of LSPR. Postmortem scanning electron microscopy (SEM) images exhibited the nanoholes fabricated together with Au NPs embedded (Fig. 2). The shapes of the nanoholes coincided with those of NPs: spherical particles gave spherical nanoholes (b-d) while triangle particles gave triangle-shaped nanoholes (e). More details will be given on site. Second, we show optothermal trapping when a single Au NP was optically heated in poly(N-isopropylacrylamide) (PNIPAM) solution.³ PNIPAM is known for its thermoresponsive nature: coil-to-globule phase transition occurs at temperatures above 32 °C (305 K). The random coil form is hydrophilic but globule form is hydrophobic, resulting in aggregation at $T > 305$ K. With laser heating of a single Au NP, we observed remarkable LSPR red-shifts ascribable to the formation of phase separated PNIPAM shell around the NP (Fig. 3). This can be regarded as optothermal trapping of PNIPAM in hot area created around the NP. Greater red-shifts were observed with increasing laser intensities. We will show the detail in the conference.

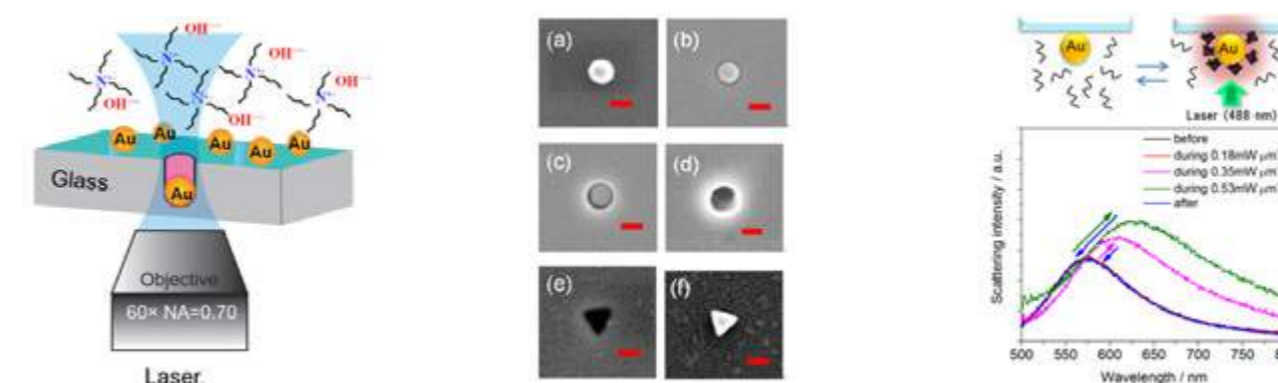


Fig. 1: Experimental setup for nanohole fabrication. Single Au NPs were illuminated with a focused laser beam at 488nm in tetra-butylammonium hydroxide, Fig. 2: Laser-induced Au NP embedding: 0 s (a), 10 s (b), 30 s (c), 30 min (d). Au triangle (e,f); 180 s (e), $3.3 \times 10^5 \text{ W cm}^{-2}$, $1.7 \times 10^5 \text{ W cm}^{-2}$ (f). Fig. 3: Optothermal trapping of PNIPAM molecules on photoexcitation of 100-nm-diameter Au nanosphere supported on glass.

References:

- [1] S. D. Brown et al. *J. Am. Chem. Soc.*, 132 (2010) 4678-468; N. S. Abadeer et al. *J. Phys. Chem. C* 120 (2016) 4691-4716.
- [2] Y. Osaka et al. *Nanoscale* 8 (2016) 18187-18196.
- [3] I. Aibara et al., *J. Phys. Chem. C* 120 (2016) 17745-17752.

Julian Gargiulo¹, Thomas Brick², Ianina L. Violi¹, Toshihiko Shibanuma², Facundo Herrera³, Félix Requejo³, Pablo Albella^{2,4}, Stefan Maier², Emiliano Cortes², Fernando D. Stefani^{1,5} // ¹Centro de Investigaciones en Bionanociencias (CIBION), Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Godoy Cruz 2390, C1425FQD Ciudad de Buenos Aires, Argentina / ²The Blackett Laboratory, Department of Physics, Imperial College London, London SW7 2AZ, United Kingdom / ³Instituto de Investigaciones Físicoquímicas Teóricas y Aplicadas (INIFTA), Dpto. de Química, FCE-UNLP, CONICET, La Plata 1900 Argentina / ⁴Instituto Universitario SIANI, Universidad de las Palmas de Gran Canaria, 35017 Las Palmas, Spain / ⁵Departamento de Física, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Güiraldes 2620, C1428EAA Ciudad de Buenos Aires, Argentina.

Amongst the various methods for patterning surfaces with colloidal NPs, optical printing is of particular interest because it does not require any previous lithographic steps. Highly focused laser beams are able to trap individual particles from solution and deliver them into a specific location upon a substrate with high accuracy and flexibility of pattern design [1]. One of the key challenges of optical printing, however, is its relatively poor ability to deposit two particles at a controllable sub-diffraction limited distance. Photo-thermal effects arising from the strong plasmonic heating of printed particles gives rise to the movement of the surrounding fluid and the generation of drag forces stronger than the optical counterparts [2]. Here, we study the optical printing lateral resolution using different combinations of substrates and NPs. We show that by using substrates of increasing thermal conductivity and by tailoring the geometry of the structures, sub-diffraction interparticle distance are attainable. Thermo-osmotic flows and thermophoresis are discussed in this context. The results presented here allow us to elucidate that the thermal gradients produced by the NPs absorbing the light create the repulsive forces that have prevented connecting identical NPs by optical printing so far. Funding by the EPSRC (EP/M013812/1) is greatly acknowledged.

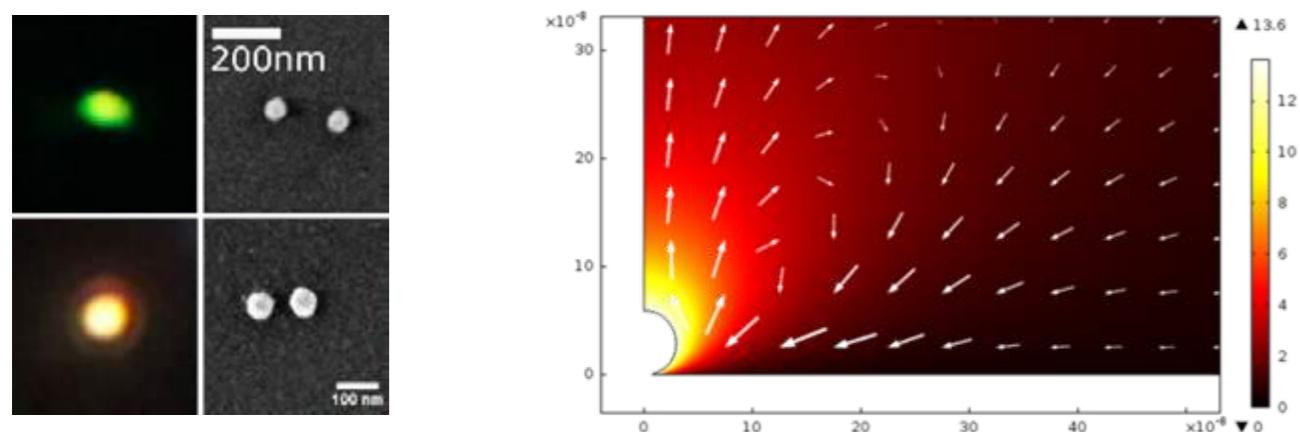


Fig. 1: Top: Dark-field and SEM image for 60 nm AuNP printed dimers. Bottom: Dark-field and SEM image for 60 nm AuNP printed next to 70 nm Au nano disk, Fig. 2: Calculated 60 nm AuNP temperature increase and subsequently induced thermo-osmotic fluid flow.

References:

- [1] Urban, A. S.; Lutich, A. a.; Stefani, F. D.; Feldmann, J. *Nano Lett.* 2010, 10 (12), 4794–4798.
[2] Gargiulo, J.; Cerrota, S.; Cortés, E.; Violi, I. L.; Stefani, F. D. *Nano Lett.* 2016, 16 (2), 1224–1229.

Yung Doug Suh^{1,2} // ¹Research Ctr. for Convergence NanoRaman Tech. (RC2NT), KRICT, DaeJeon, Korea / ²School of Chemical Engineering, SungKyunKwan University (SKKU), Suwon, Korea.

Raman scattering can provide a wealth of molecular chemical information, but it is basically a highly inefficient inelastic light scattering process between photon and molecule with a very small cross-section. Raman scattering signals are often poorly reproducible, meaning that very strong and controllable amplification mechanism, such as SERS (Surface-Enhanced Raman Scattering) or NERS (Nanogap-Enhanced Raman Scattering), is needed to obtain measurable and reliable Raman signals.

Plasmonically coupled metallic nanostructures with ultra-small (~1 nm or smaller) nanogaps can generate very strong and controllable electromagnetic fields that can generate strong NERS signals from Raman dyes inside the nanogap. Therefore, plasmonic nanogap-enhanced Raman scattering (NERS) can be defined as Raman scattering signal enhancement from plasmonic nanogap with ~1 nm gap size.

In this talk, I will overview recent breakthroughs, advances, and application of plasmonic nanogap-enhanced Raman scattering (NERS) with metal nanogap particles revealed by single-molecule / single-particle-level Nano Raman spectroscopy showing that these plasmonic nanogap particles can generate ultra-strong, quantifiable Raman signals in a highly reproducible manner.

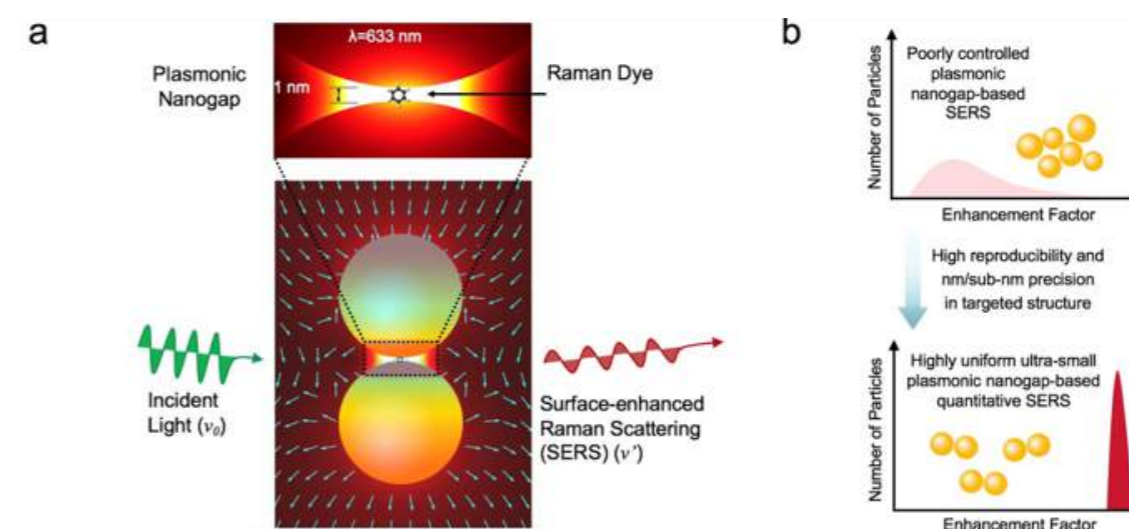


Fig. 1: (a) Highly-enhanced electromagnetic (EM) fields in the 1nm gap of a plasmonic dimer, (b) Fulfilling BOTH high surface-enhanced Raman scattering (SERS) enhancement factor (EF) AND narrow EF distributions to make SERS signals detectable, linear, thus quantitative, toward practical real-world biomedical/clinical applications like in the case of UV-Vis absorption or fluorescence emission.

References:

- [1] H. Lee, S.M. Jin, H.M. Kim, and Y.D. Suh, *Phys. Chem. Chem. Phys.* (invited review article), 15 (2013) 5276-5287
[2] D. Lim, K.-S. Jeon, H.M. Kim, J.-M. Nam, and Y.D. Suh, *Nature Materials*, 9 (2010) 60-67.
[3] J.-H. Lee, J.-M. Nam*, K.-S. Jeon, D.-K. Lim, H. Kim, S. Kwon, H. Lee, Y.D. Suh, *ACS Nano*, 11 (2012) 9574-9584
[4] H. Lee, G.-H. Kim, J.-H. Lee, N.H. Kim, J.-M. Nam, and Y.D. Suh, *Nano Letters*, 15 (2015) 4628-4636
[5] J.-M. Nam, J.-W. Oh, H. Lee, and Y.D. Suh, *Acc. Chem. Res.* 49 (2016) 2746-2755.

Dana Cialla-May, Karina Weber, Jürgen Popp // Leibniz Institute of Photonic Technology, Albert-Einstein-Str. 9, 07745 Jena, Germany / Friedrich Schiller University Jena, Institute of Physical Chemistry and Abbe Center of Photonics, Helmholtzweg 4, 07743 Jena, Germany / InfectoGnostics Research Campus Jena, Centre for Applied Research, Philosophenweg 7, 07743 Jena, Germany

Due to the molecular specificity and potential single-molecule sensitivity surface-enhanced Raman spectroscopy (SERS) gained much attention in life sciences and medical applications. [1] Therefore, powerful SERS substrates are needed which are feasible via bottom-up, self-organization and top-down fabrication strategies. [2]

Here, we report on a microfluidic platform allowing for high-throughput and reproducible measurement conditions and the application in drug and metabolite monitoring will be introduced. Levofloxacin, an antibiotic administered for urinary tract infections was successfully detected in spiked patient urine samples showing the high potential of SERS in medical detection schemes. [3] As a further example the quantification of nitroxoline is achieved by using the standard addition method as illustrated in Figure 1 [4]. A detection limit of 0.57 mg/L and a quantification limit of 1.23 mg/L were found. The linear range is between 0.81 and 8.13 mg/L, covering the minimum inhibitory concentration of the most commonly encountered uropathogens. Moreover, SERS-based methods are suitable in food and environmental relevant analytics as shown by the detection of Sudan III within the background of paprika powder [5] and azorubine (E122) in commercial available drinks with varying complexity [6] as well as label-free detection of quarantine organisms [7]. Finally, the potential of SERS in bioanalytical detection schemes is also demonstrated by the cartridge-based detection of sulfamethoxazole in water samples [8].

The project "Exasens" (13N13856) is funded by the Federal Ministry of Education and Research, Germany (BMBF). The project "InfectoGnostics" (13GW0096F) is funded by the Development Bank of Thuringia and the European Union (EFRE).

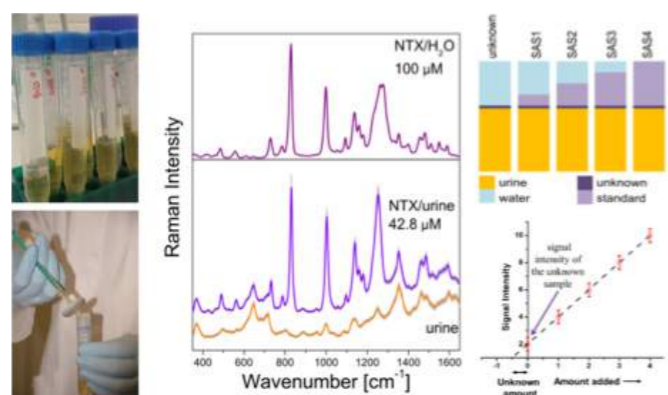


Fig. 1: SERS-based investigation of nitroxoline in spiked human urine samples. The quantification is achieved by employing the standard addition method.

References:

- [1] Cialla et al. (2014) *Nanophot.*, 3, 383. [2] Jahn et al. (2016) *Analyst*, 141, 756. [3] Hidi et al. (2016) *JPCC*, 120, 20613. [4] Hidi et al. (2016) *Anal. Chem.*, 88, 9173. [5] Jahn et al. (2015), *Anal. Chim. Acta*, 860, 43. [6] Peksa et al. (2015), *Anal. Chem.*, 87, 2840. [7] Yüksel et al. (2015), *Analyst*, 140, 7254. [8] Patze et al. (2017) *Anal Chim Acta*, 949, 1.

Zsuzsanna Heiner^{1,2}, Marina Gühlke², Vesna Živanovic^{1,2}, Fani Madzharova², Janina Kneipp^{1,2} // ¹School of Analytical Sciences Adlershof, Humboldt Universität zu Berlin, Albert-Einstein-Str. 5-11, 12489 Berlin, Germany / ²Department of Chemistry, Humboldt Universität zu Berlin, Brook-Taylor-Str 2, 12489 Berlin, Germany

Combination of surface enhanced Raman scattering (SERS) with its two-photon analogue, surface enhanced hyper-Raman scattering (SEHRS), provides complementary structural and chemical information due to the different corresponding selection rules. Depending on the molecular symmetry, SEHRS may probe IR active modes or additional "silent" modes, which are seen neither in Raman nor in IR spectra [1]. In a SEHRS experiment, thanks to the near infrared excitation, deeper penetration and femtoliter-range probed volume can be achieved, resulting in an improved resolution for imaging compared with SERS. Because technically SERS and SEHRS can be detected quasi-continuously within one micro-spectroscopic setup, it is straightforward to combine these complementary methods to study nanoparticle-molecule interactions [2, 3]. When applying multivariate signal processing techniques (e.g., hierarchical cluster analysis, HCA, or principal component analysis, PCA) to one- and two-photon excited SERS spectra, the sensitivity in the analysis can be substantially increased [4].

Here, we investigated the SEHRS and SERS spectra and the spatial distributions of crystal violet (CV) and malachite green (MG) on immobilized plasmonic surfaces. Each sample type consisted of two connected regions, either a CV and CV-MG-mixture or an MG and CV-MG-mixture, respectively. The SERS and SEHRS spectra were recorded by scanning many small, microscopic areas across the border regions and also at the distinct non-border regions on both sides on a macroscopic (millimeter) scale. Because CV and MG structurally differ only in one dimethylamino group, their one- and two-photon excited spectra exhibit a high degree of similarity. To utilize all of the spectral differences between the spectra of the studied dyes and their mixtures, we successfully applied PCA to map the distribution of the molecules. The presented hyperspectral mapping technique constitutes a novel method for multiplex imaging of complex biological systems. As the first real demonstration of this hyperspectral imaging, we show that combined SERS and SEHRS fingerprints can also be collected and studied from single living cells which will help SEHRS hyperspectral imaging to become an important new direction in future all-optical nanosensing as well as in nanobiophotonics.

Financial Support by ERC Starting Grant no.259432 (MULTIBIOPHOT) to J.K. and M.G. and DFG (GSC 1013 SALSA) to Z.H. and V.Ž. is gratefully acknowledged. F.M. acknowledges funding by a Chemiefonds Fellowship (FCI).

References:

- [1] Kneipp J, Kneipp H, Kneipp K, *PNAS*, 103 (2006) 17149-17153. [2] Gühlke M, Heiner Z, Kneipp J, *Phys. Chem. Chem. Phys.*, 17 (2015) 26093-26100. [3] F. Madzharova, Z. Heiner, J. Kneipp. *J. Phys. Chem. C*, 121 (2017) 1235-1242. [4] M. Gühlke, Z. Heiner, J. Kneipp, *Phys. Chem. Chem. Phys.*, 18 (2016) 14228-14233.

Martin Werts // Ecole normale supérieure de Rennes and CNRS, lab. SATIE, Av. R. Schuman, F-35170 Bruz, France

The bottom-up approach for making functional nanostructures via self-assembly in solution leads to objects that are usually represented pictorially using idealised models. These models are then validated against experimental observations (microscopy, spectroscopy), often of static nature. As part of our work on plasmonic assemblies, we have been fascinated by the dynamic behaviour of these nano-assemblies in solution, at equilibrium (Brownian fluctuations) and away from equilibrium. These dynamics not only yield information on the shape of the objects in solution (via diffusion and sedimentation), and their evolution over time, but can also help in extracting quantitative spectroscopic data, when coupled to optical spectroscopy.

Fluorescent ligand molecules that bind to the surface of plasmonic particles were found to give insight in dynamics of the molecular capping layer, and show that the gold-thiol bond is not always very robust.[1] These ligand molecules were instrumental in quantifying fluorescence quenching by metal nanoparticles.[2] The optical resonances of the plasmonic particles themselves, which can be read out via light extinction, scattering[3] and intrinsic photoluminescence,[4] also convey information about the structure of particle assemblies, e.g. DNA-linked structures. We furthermore use microfluidic architectures to set up concentration gradients[5] and electric fields,[6] probing the diffusion coefficient and the electrokinetic response of the particles. Using bright-field and dark-field microscopy we can study the dynamics of plasmonic nanoparticle assemblies at the ensemble level and at the single-particle level.

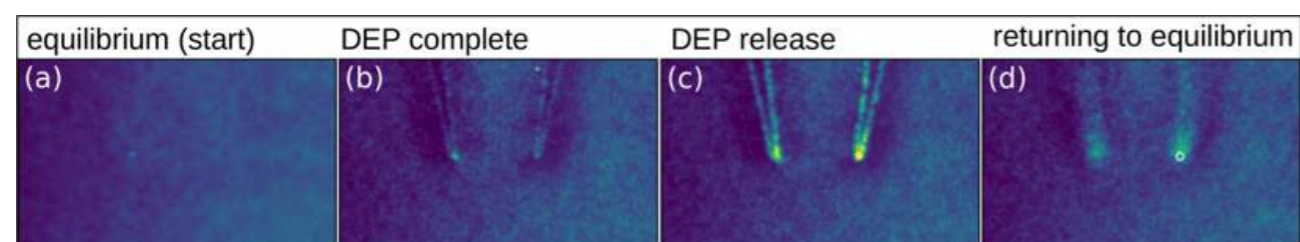


Figure: False-colour, cycle-averaged dark-field microscopic images of the dielectrophoretic (DEP) capturing of 150 nm diameter gold nanoparticles in water, and subsequent release. The width of each image is 100 μm .

References:

- [1] M. Loumagne, R. Praho, D. Nutarelli, M. H. V. Werts, A. D barre, *Phys. Chem. Chem. Phys.* 12 (2010) 11004
- [2] J. R. G. Navarro, M. Plugge, M. Loumagne, A. Sanchez-Gonzalez, B. Mennucci, A. D barre, A. M. Brouwer, M. H. V. Werts, *Photochem. Photobiol. Sci.* 9 (2010) 1042
- [3] M. Loumagne, C. Midelet, T. Doussineau, P. Dugourd, R. Antoine, M. Stamboul, A. D barre, M. H. V. Werts, *Nanoscale* 8 (2016) 6555
- [4] M. Loumagne, G. Laurent, M. H. V. Werts, A. D barre, *Phys. Chem. Chem. Phys.* 18 (2016) 33264
- [5] M. H. V. Werts, V. Raimbault, R. Texier-Picard, R. Poizat, O. Fran ais, L. Griscom, J. R. G. Navarro, *Lab Chip* 12 (2012) 808
- [6] M. H. V. Werts, F. Allix, O. Francais, C. Frochot, L. Griscom, B. Le Pioufle, M. Loumagne, J. Midelet, *IEEE J. Sel. Top. Quantum Electron.* 20 (2014) 6900613

Mathias Brust and Marcin Grzelczak // Department of Chemistry, University of Liverpool, Liverpool L69 7ZD, United Kingdom

Charge transfer across biological membranes is the basis for many fundamental processes of life such as photosynthesis, the respiratory chain, ATP synthesis and neuronal signaling, to name a few. Since electroneutrality has to be maintained, transfer of positive and negative charge are not independent of each other but are energetically coupled. If mechanistically only one type of charge carrier can transfer the membrane, say as potassium ions through a specific channel, the transfer of a small number of ions leads to a build-up of a membrane potential, which prevents further transfer. While there are many natural and artificial charge carriers and ion channels there appears to be only preliminary evidence for the ability of metal nanoparticles to act as ion transfer mediators.[1]

Metallic particles do not occur naturally in biological systems and, besides ion transfer, offer mechanistically completely new routes of charge transfer across membranes, namely by direct metallic conduction of electrons. In nature, electron-transfer across or along membranes is mediated by small redox molecules, often quinones, which carry electrons between redox-proteins resident in the membrane. In principle, a metal particle could be far more efficient and act as a trans-membrane nanowire, provided that there are feasible mechanisms of heterogeneous electron transfer between the metal particle and the aqueous medium on both sides of the membrane. Future hybrid systems could benefit from the ability to "wire-up" cells or micro-organisms by enabling metallic conduction of electrons across their membranes.

Here I will give an account of our current efforts in the development of ion and electron transfer systems based on gold nanoparticles. In particular, I will discuss gold nanoparticles capped with mercapto-carboranes, which selectively shuttle certain ions across supported phospholipid bilayers in an electrochemical cell and across the membrane of phospholipid vesicles. Charge transfer was either measured directly in potential step experiments, or indirectly by monitoring changes in membrane potential of the vesicle membrane by fluorescence spectroscopy. Coupled ion and electron transfer as a means of biomimetic energy conversion will be discussed.

Funding by the ERC Advanced Grand, project 321172 PANDORA, is gratefully acknowledged.

References:

- [1] Marcin P. Grzelczak, Alexander P. Hill, Domagoj Belic, Dan F. Bradley, Casper Kunstmann-Olsen and Mathias Brust. *Faraday Discuss.*, 2016,191, 495-510.

Robin Schürmann, Ilko Bald // Department of Chemistry, University of Potsdam, Karl-Liebknecht-Str. 24-25, 14476 Potsdam, Germany, BAM Federal Institute for Materials Research and Testing Richard-Willstätter-Str. 11, 12489 Berlin, Germany

In cancer photothermal therapy (PTT) the plasmonic heating of laser illuminated gold nanoparticles (GNPs) is exploited to destroy tumorous tissue [1]. The irradiation of GNPs with ns-laser pulses induces a fragmentation of DNA nucleobases into its smallest subunits in close proximity to the particle most likely caused by the extremely high temperatures on the GNP surface [2]. Furthermore, low energy electrons (LEEs), which are strongly reactive towards the halogenated nucleobases 5-bromouracil or 8-bromo-adenine (8BrA), are generated by thermionic emission from the GNP at high laser fluences. Due to the attachment of a LEE such nucleobase analogues form transient negative ions that subsequently dissociate, favorably by cleavage of the C-Br bond, forming radicals that might act as a precursor for DNA single strand breaks (SSB). 8BrA containing DNA strands show an enhanced SSB cross section towards LEEs compared to its native counterparts. Using surface enhanced Raman scattering (SERS) the decomposition products of DNA nucleobase analogues on laser illuminated GNPs can be monitored [3]. Even under illumination with low intensity continuous wave lasers in a typical SERS setup 8BrA rapidly dissociates into adenine mediated by a dissociative electron transfer from the plasmonic nanoparticles [4]. Beside the potential applications for PTT, such reactions need to be taken into account in the interpretation of SERS spectra of electrophilic molecules.

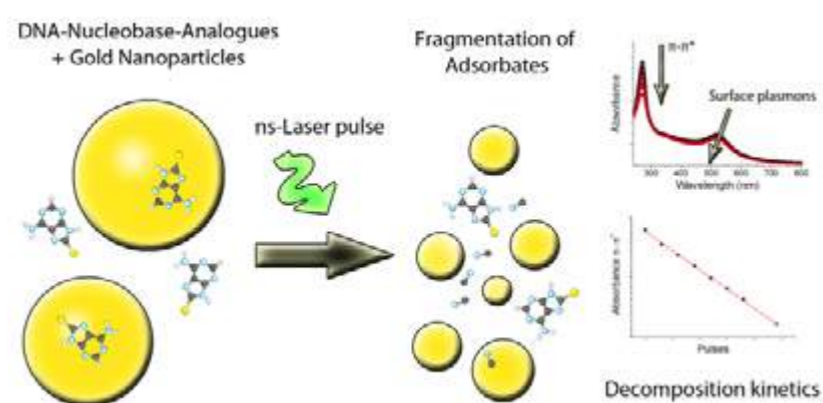


Figure 1: Illustration of the fragmentation of 8BrA on pulsed laser illuminated GNP and the determination of the decomposition kinetics with UV-Vis-Spectroscopy. Image adapted from source [2]

References:

- [1] N. S. Abadeer and C. J. Murphy, *J. Phys. Chem. C*, 2016, 120 (9), pp 4691–4716
- [2] R. Schürmann and I. Bald, *PCCP*, accepted DOI: 10.1039/C6CP08433H
- [3] R. Schürmann and I. Bald, *J. Phys. Chem. C*, 2016 120 (5), pp 3001–3009
- [4] R. Schürmann and I. Bald, *Nanoscale*, 2017,9, 1951-1955

Weichun Zhang, Martin Caldarola, Biswajit Pradhan, Michel Orrit // Huygens-Kamerlingh Onnes Laboratory, Leiden University, 2300 RA Leiden, The Netherlands

Redox reactions are central to energy conversion and life metabolism. We present electrochemical measurements with fluorescent readout of the redox-sensitive dye Methylene Blue (MB, Fig. 1), at the single-molecule level. To overcome the low fluorescence quantum yield of MB we enhanced fluorescence by individual gold nanorods [1] to achieve the required sensitivity (Fig. 2). By measuring the same molecule at different electrochemical potentials we determined the mid-point potential of each single molecule through its redox-induced fluorescence blinking dynamics. Figure 3 shows three time traces (binned to 1ms) obtained from the same molecule at different potentials successively. The blinking dynamics is evidently responding to the electrochemical potential. Our technique could be applied to measure the local redox potential in chemical or biological systems by single molecules.

Funding by the Netherlands Organization for Scientific Research (NWO) is gratefully acknowledged.

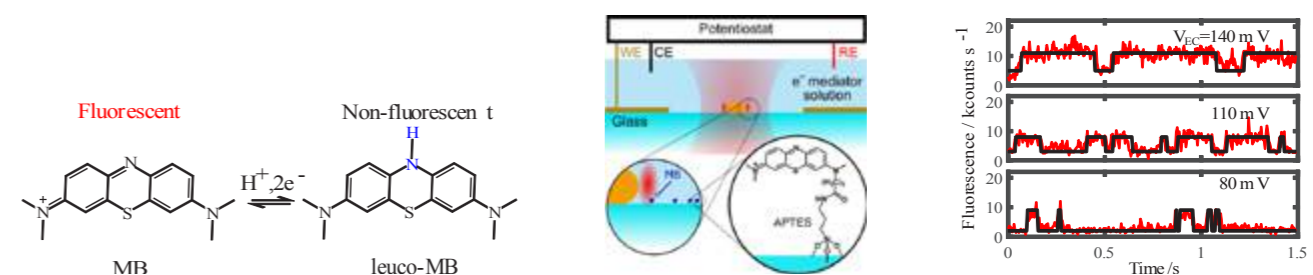


Fig. 1: Two-electron reduction/oxidation reaction of Methylene Blue (MB). The reduced species, leuco-Methylene Blue is non-fluorescent under visible excitation, Fig. 2: Scheme of the combined electrochemical-confocal setup and sample. Individual AuNRs (not to scale) and MB molecules are immobilized on the glass surface, Fig. 3: Fluorescence time traces of the same single molecule at different potentials, where different blinking dynamics can be seen.

References:

- [1] H. Yuan, S. Khatua, P. Zijlstra, M. Yorulmaz, M. Orrit, *Angewandte Chemie International Edition*. 2013, 52, 1217-1221.
- [2] W. Zhang, M. Caldarola, B. Pradhan, M. Orrit, *Angewandte Chemie International Edition*. 2017, DOI: 10.1002/anie.201612389.

Maria Dienerowitz, Thomas Heitkamp, Hendrik Sielaff, Michael Börsch // Single-Molecule Microscopy Group, Jena University Hospital, University of Jena, 07743 Jena / Abbe Center of Photonics (ACP), 07743 Jena, Germany

Brownian motion renders observing dynamic behaviour of biomolecules in solution beyond tens of milliseconds a challenging task. Most techniques rely on immobilisation or transient diffusion through a confocal laser focus. We present an Anti-Brownian Electrokinetic trap [1-3] to increase the observation time of individual proteoliposomes, DNA origami and nanoparticles [4]. We are able to trap single 10 nm silver spheres up to a minute and biomolecules labeled with a single fluorophore beyond 2 s. The ABELtrap is an active feedback system cancelling the nanoparticle's Brownian motion by applying an electric field. We show how the induced electrokinetic force confines the motion of nanoparticles and biomolecules to the centre of the trap. We are particularly interested in the conformational dynamics of individual FoF1-ATP synthase proteins. Monitoring sequential distance changes between two specifically attached dyes using single-molecule FRET allows us to observe this membrane-bound rotary protein in real time.

This work was supported in part by the Thuringian State Government within its ProExcellence Initiative (ACP2020) and DFG grant BO1891/16-1.

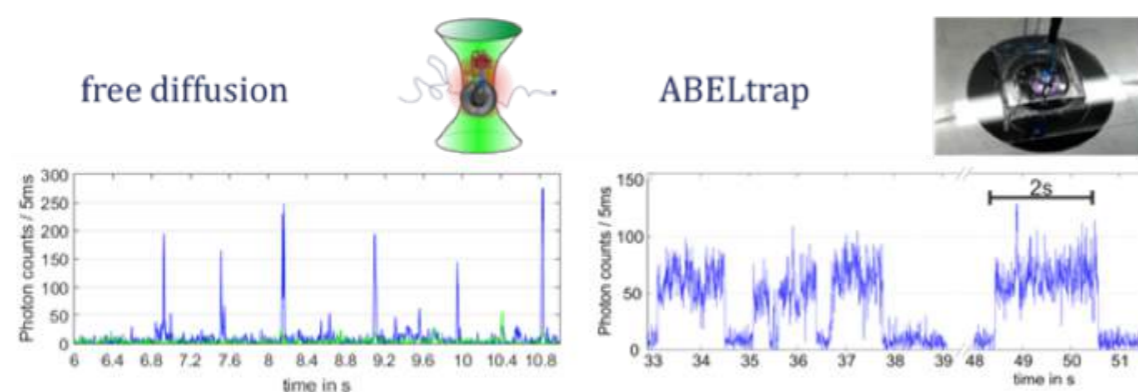


Fig. 1: The observation time of FoF1-ATP synthase molecules (*E. coli*, reconstituted in liposomes) increases from tens of ms for free diffusion through a laser focus to seconds holding the proteoliposome in an ABELtrap. A trap event starts with the sudden increase of emitted photons from the excited fluorophore and ends with fluorophore blinking or bleaching. We label each FoF1-ATP synthase with a single mNeonGreen fluorophore at the α -subunit of the rotor protein.

References:

- [1] AE Cohen and WE Moerner, PNAS 12 (2006), 4362,
- [2] A Fields and AE Cohen, PNAS 108 (2011), 8937,
- [3] Q Wang and WE Moerner, Nat. Methods 11 (2014), 555,
- [4] M. Dienerowitz et al., Proc. SPIE 9714 (2016), 971402.

DYNAMICS

Weixiang Ye^{1,2}, Laura Tüting^{1,2}, Rubén Ahijado-Guzmán¹, and Carsten Sönnichsen¹ // ¹Institute of Physical Chemistry, University of Mainz, Duesbergweg 10-14, D-55128 Mainz, Germany / ²Graduate School Materials Science in Mainz, Staudinger Weg 9, D-55128 Mainz, Germany

The quantification of dynamical processes in biological molecules (e.g. DNA or proteins) is an essential step towards understanding biological processes. Currently, relevant techniques for the study of single-molecule dynamics are FRET (Förster or fluorescence resonance energy transfer)¹ and optical tweezers.² However, FRET relies on fluorescent dyes, where bleaching and blinking limit the measured time. On the other hand, optical tweezers require the use of long linkers which could affect the dynamics of the system. Coupled plasmonic nanoparticles ('plasmon rulers') offer an alternative without those limitations. In 2005, this concept was demonstrated and applied to study the hybridization of DNA macromolecules³. More recently, this method was used for probing DNA stiffness⁴.

Here, we present the characterization of the folding dynamics and stiffness of multiple single polyethylene glycol (PEG) molecules at once by using fast spectral imaging single-particle plasmon spectroscopy. The spectral imaging method allows to measure on multiple plasmon ruler simultaneously which drastically improves statistics, a key aspect for single molecule research. Our study is the first time plasmon rulers are applied to study polymer dynamics.

Acknowledgment:

This work was financially supported by the ERC grant 259640 ("SingleSens"). L.T and W.Y. are recipients of DFG fellowships through the Excellence Initiative by the Graduate School Materials Science in Mainz (GSC 266).

References:

- [1] Mickler, M.; Hessling, M.; Ratzke, C.; Buchner, J.; Hugel, T. Nature Structural & Molecular Biology 2009, 16 (3), 281-286.
- [2] Jahn, M.; Rehn, A.; Pelz, B.; Hellenkamp, B.; Richter, K.; Rief, M.; Buchner, J.; Hugel, T. Proceedings of the National Academy of Sciences 2014, 111 (50), 17881-17886.
- [3] Sönnichsen, C.; Reinhard, B. M.; Liphardt, J.; Alivisatos, A. P. Nature Biotechnology 2005, 23 (6), 741-745.
- [4] Chen, T., Hong, Y., & Reinhard, B. M. Nano letters 2015, 15(8), 5349-5357.

Hana Šípová, Lei Shao, Nils Odebo Länk, Mikael Käll // Department of Physics, Chalmers University of Technology, S-412 96 Göteborg, Sweden

Light can exert a force on matter by means of momentum exchange through both absorption and scattering, enabling fast and precise movement control of small objects [1]. Noble metal nanostructures that support localized surface plasmon resonances (LSPRs) enhance light-matter interaction and therefore can be manipulated using wireless and contactless laser tweezers. Here we use circularly polarized laser light to drive ultrafast spinning of plasmonic gold nanorods in solution through optical torques dominated by tunable resonant light scattering (Figure 1a) [2]. By analysis of rotational dynamics of the trapped nanorods, we measured thicknesses of biomolecular layers adsorbed on their surface, such as self-assembled monolayers of alkanethiols and single- and double-stranded DNA (dsDNA), with a sub-nanometer resolution. Moreover we were able to distinguish DNA molecules of the same length, but different conformation (Figure 1b). The temperature of the surface of the nanorod can be increased by plasmonic heating to approach the melting temperature of the dsDNA. Thus, by tracking the rotational frequency in real time, the temperature-dependent dissociation kinetics of DNA duplexes were observed (Figure 1c). We believe, that the method developed here opens vast possibilities to probe various biomolecular interactions on a nanoscale, as well investigation of biomolecular films, temperature-induced changes of biomolecules, and ultra-sensitive biomolecular detection.

Funding by the Knut and Alice Wallenberg Foundation and the Swedish Research Council is gratefully acknowledged

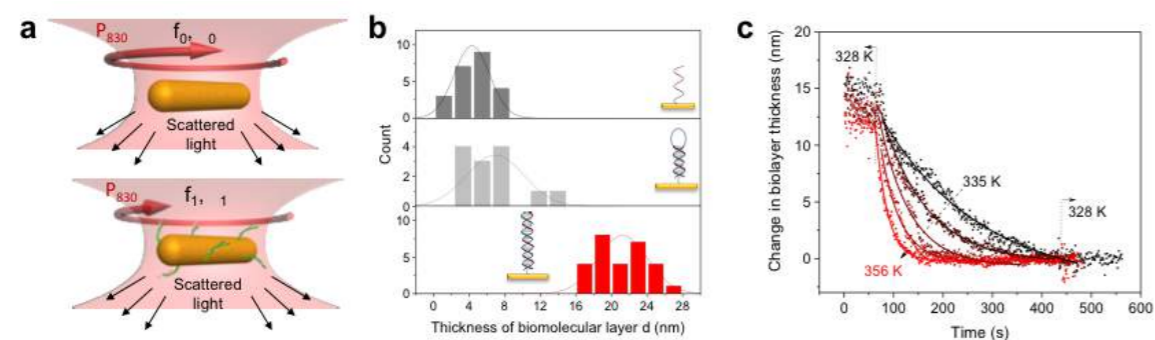


Figure 1: a) Adsorption of biomolecular layer slows down rotation and rotational Brownian motion of nanorod in an optical trap. b) Measured thickness of DNA layers. c) Temperature-dependent kinetics of DNA dissociation on individual gold nanorods.

References:

- [1] Friese, M.E.J., et al., Nature, (1998). 395(6702): p. 621-621.
- [2] Shao, L., et al., (2015). 9(12): p. 12542-12551.

POSTER

- 25 | **Gold Bipyramids performing as Dual-Modal Optical Immunosensors** // Andreea Campu
- 26 | **How irreversible is SERS exactly?** // G. Charron
- 27 | **Plasmonic Nanoruler based on Light Emitting Tunneling Junctions** // André Dathe
- 28 | **Core-shell structures as precursors for nanodiamonds: TERS on TNT-RDX nanocomposites** // Tanja Deckert-Gaudig
- 29 | **SERS sensing strategies for bioanalytical applications** // Vera Dugandžic
- 30 | **Gold nanostructures decorated with aptamers as LSPR and SERS detectors of ochratoxin A** // Betty C. Galarreta
- 31 | **Entropically Driven-Fully Reversible Aggregation of Plasmonic Gold Nanoparticles Coated in 18-C-6-CH₂-SH** // Alex Hill
- 32 | **Implications of Chemical Interactions Between Tip and Analyte in TERS – A Quantum Chemical Approach** // Daniel Kinzel
- 33 | **Nanostructures** // F. Madzharova
- 34 | **Mapping electromagnetic field distributions by photoinduced force microscopy** // Robert Meyer
- 35 | **Analysis of dielectrophoretic trapping of functionalized gold nanoparticles in liquid solution** // Clyde Midelet
- 36 | **Usage of the plasmonic effect for heterogeneous catalysis** // Heike L.K.S. Mosch
- 37 | **Fabrication of glass microspheres doped with metallic nanoparticles and quantum dots for Whispering Gallery Mode resonators** // Rafał Nowaczynski
- 38 | **System for exciting WGM microresonators** // Piotr Paszke
- 39 | **Plasmonic properties of spherical metallic nanoparticles for effective absorption of solar radiation and their heating** // Victor K. Pustovalov
- 40 | **Nanoscale localisation of a Candida albicans peptide-toxin on cell membranes by TERS** // Ludovic Roussille
- 41 | **Tilted metal nanocone metasurfaces as waveguide couplers** // Janne Simonen
- 42 | **Ligand exchange of Gold NanoCubes for Biosensing Application** // Chandan Singh
- 43 | **Self-organized plasmonic metals formation in limited volume matrixes** // Vladimir Sivakov
- 44 | **Characterization of the protein corona formation of nanoparticles in artificial systems and living cells** // Gergo Peter Szekeres
- 45 | **DNA-manipulation and detection based on plasmonic effects** // Sophie Thamm
- 46 | **Imaging Tip-enhanced Raman Spectroscopy (iTERS) – a new efficient method for fast TERS imaging** // Steffen Trautmann
- 47 | **SERS study of the roles of metal ions on photo-induced dimerization of p-Aminothiophenol on gold nanoparticles** // Zhiyang Zhang
- 48 | **SERS investigation of liposomal-AuNP drug delivery systems** // Vesna Živanovic
- 49 | **Hyperspectral imaging of plasmon resonances for biosensing** // David Zopf
- 50 | **Detection of the Pseudomonas aeruginosa metabolite pyocyanin by SERS combined with a microfluidic platform** // Olga Žukovskaja

GOLD BIPYRAMIDS PERFORMING AS DUAL-MODAL OPTICAL IMMUNOSENSORS

Andreea Campu¹, Monica Focsan¹, Frederic Lerouge², Stephane Parola², Dana Maniu³, Simion Astilean^{1,3} //

¹Nanobiophotonics and Laser Microspectroscopy Center, Interdisciplinary Research Institute on Bio-Nano-Sciences, Babes-Bolyai University, Treboniu Laurean Str. 42, Cluj-Napoca 400271, Romania / ²Ecole Normale Supérieure de Lyon, CNRS, Université Lyon 1, Laboratoire de Chimie UMR 5182, 46, allée d'Italie, F-69364, Lyon Cedex 07, France. / ³Biomolecular Physics Department, Faculty of Physics, Babes-Bolyai University, M Kogalniceanu Str. 1, Cluj-Napoca 400084, Romania

The development of nanosensors able to detect various specific biomarkers with a very high sensitivity, selectivity and reliability represents an urgent requirement for implementation of early medical diagnostic in nanomedicine. Anisotropic gold nanoparticles, due to their unique optical properties [1], including spectral sensitivity of localized surface plasmon resonance (LSPR) to the dielectric properties of environment and the presence of enhanced electromagnetic field to sustain surface enhanced Raman scattering (SERS) activity, have recently started to be investigated as LSPR-SERS plasmonic-based dual immunoassays, enabling both the sensitive and specific ultradetection of targeted analytes as well transduction and analysis of antigen-antibody recognition interaction.

Herein, we present a “proof-of-concept” for the feasibility of detecting the specific biotin-streptavidin interaction via a new LSPR/SERS-active platform based on gold bipyramidal-shaped nanoparticles (AuBipi) functionalized with biotin molecules as recognition element. Firstly, in order to confirm functionalization of AuBipi with biotin and further interaction of streptavidin, the biotin molecules have been labelled with p-Aminothiophenol (p-ATP) which, due to thiol group, can be grafted onto the AuBipi surface and provide reliable SERS information as Raman reporter probe [2] about the immobilized recognition element for streptavidin detection. While the capture of streptavidin onto the p-ATP@Biotin- AuBipi surface can be monitored by the recorded red-shift of the LSPR of AuBipi, the SERS technique -due to its fingerprinting capabilities, convey information via specific Raman bands of streptavidin at 1008, 1415 cm⁻¹ (Trp) and 1224 cm⁻¹ (Amide III) alongside with characteristic Raman bands of p-ATP at 1081 and 1591 cm⁻¹. Additionally, the specific recognition interaction was also confirmed by independent measurement via FT-IR spectra and simulation. Furthermore, by monitoring the SERS bands of p-ATP, a limit of detection (LOD) of 10⁻⁹ M of streptavidin was achieved.

Our design could provide a reference for further immunoassay designs for real-time detection of relevant biomarkers.

Funding by the CNCS-UEFISCDI Romania, under the project number PN-II-PT-PCCA-2013-4-1961, is gratefully acknowledged.

References:

- [1] M. Liu et al., Physical Review B 76 (2007) 235428.
[2] M. Baia et al., Chem. Phys. Lett. 422 (2006) 127-132.

G. Brackx², G. Charron¹, A. Gélabert², M. Benedetti², J. Gaillardet² // ¹Matter and Complex System (MSC) Laboratory, Paris-Diderot University, Paris, 75205, France / ²Institut de Géophysique du Globe de Paris (IPGP), Paris, 75238 cedex 05, France

Surface Enhanced Raman Scattering (SERS) displays striking advantages for quantitative analysis in the fields of biomedical diagnosis, food control and environmental monitoring. On principle, its high sensitivity allows for performing measurements without pre-concentrating the sample, while its high specificity enables the identification of target analytes in complex matrices. Despite these features, SERS still has to overcome a few challenges before turning into a routine analytical method. Amongst those is its notorious lack of reproducibility. Very often, SERS substrate samples prepared following apparently identical protocols give very different spectral intensities. Their selection for further spectroscopic investigation is governed by the “If it works, use it. If not, throw it away” paradigm.

In this study, we will characterise by statistical analysis how irreproducible exactly SERS is, on the case of a simple sensor of a heavy metal ion involving randomly aggregated silver colloids. Critically, we will determine what analytical performances one can expect from such typically irreproducible system. We will show that despite highly variable intensities, appropriate signal processing affords performances that are still competitive for environmental monitoring.

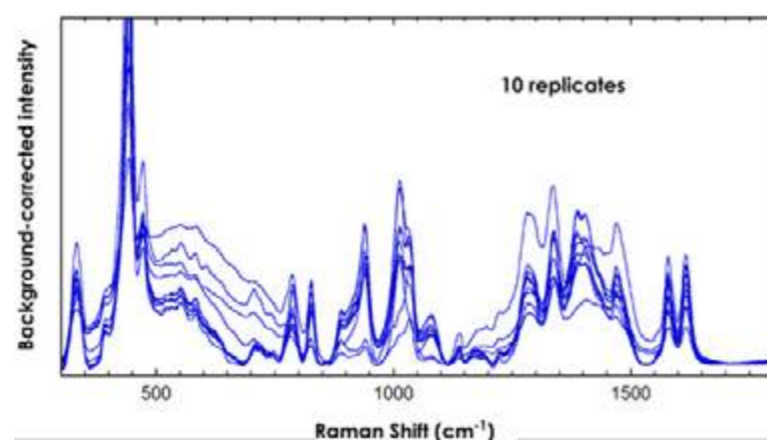


Figure 1: Typical variability of SERS signal in our sensor based on randomly aggregated Ag colloids.

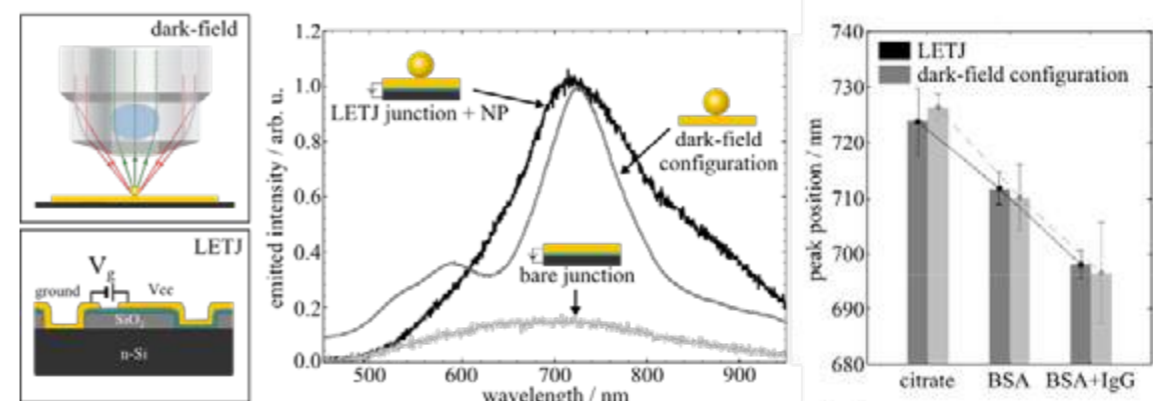
References:

[1] Halvorson, R. A. & Vikesland, P. J. Surface-Enhanced Raman Spectroscopy (SERS) for Environmental Analyses. *Environ. Sci. Technol.* 44, 7749–7755 (2010).
 [2] Álvarez-Puebla, R. A. & Liz-Marzán, L. M. Environmental applications of plasmon assisted Raman scattering. *Energy Env. Sci* 3, 1011–1017 (2010).
 [3] Wang, Y., Yan, B. & Chen, L. SERS Tags: Novel Optical Nanoprobes for Bioanalysis. *Chem. Rev.* 113, 1391–1428 (2013).
 [4] Cheung, W., Shadi, I. T., Xu, Y. & Goodacre, R. Quantitative Analysis of the Banned Food Dye Sudan-1 Using Surface Enhanced Raman Scattering with Multivariate Chemometrics†. *J. Phys. Chem. C* 114, 7285–7290 (2010).

André Dathe, Mario Ziegler, Uwe Hübner, Wolfgang Fritzsche, Andrea Csaki, Ondrej Stranik // Leibniz Institute of Photonic Technologies, Albert-Einstein-Str. 9, 07745 Jena, Germany

Conformational changes and intramolecular distances of single biomolecules are of high interest in bioanalytics and plasmonic systems for analysis are getting more and more complex[1]. Rulers based on fluorescent labels are already applied in DNA detection[2], but suffer from bleaching. Plasmonic nanorulers which utilize pairs of metal nanoparticles[3] overcome some shortcomings, but they require cumbersome optical dark-field configurations. In the presented plasmonic ruler, we implement a different geometry consisting of a metal layer and metal nanoparticles, which exhibits a characteristic localized plasmon mode induced by electromagnetic coupling, known as ‘gap mode’[4-7].

Beside excitation by external light illumination, plasmons can also be excited by beams of electrons[8]. Combining all ideas, we achieved to excite gap modes by applying electrical current in a modified material stack as substrate – introducing Light Emitting Tunneling Junctions (LETJ)[9] – and use this system as a nanoruler[10]. The research addresses pending problems of some plasmonic sensors – miniaturization and parallelization – by transiting the usual optical excitation of surface plasmons into integrable chips produced on semiconductor wafer-scale which provides a way for easy to miniaturize sensors compatible to integrated and opto-electrical circuits.



References:

[1] O. Stranik et al., ‘Development of new classes of plasmon active nano-structures and their application in bio-sensing and energy guiding’, *Front. Phys.*, 9, 652, 2014
 [2] C. Sönnichsen et al., ‘A molecular ruler based on plasmon coupling of single gold and silver nanoparticles’, *Nature Biotechnology* 23,6, June 2005
 [3] A. Csáki et al., ‘Plasmonic nanoparticle synthesis and bioconjugation for bioanalytical sensing’. *Eng. Life Sci.*, 15, 266–275, 2014
 [4] J. Mock et al., ‘Distance-Dependant Plasmon Resonant Coupling between a gold nanoparticle and gold film’, *Nano Letters*, 8,8, 2245, 2008
 [5] G. Hajisalam, ‘Probing the Quantum Tunneling limit of Plasmonic Enhancement by Third Harmonic Generation’, *Nano Letters* 14, 6651, October 2014
 [6] C. Huang et al., ‘High Order Gap Modes of Film-Coupled Nanosphere’, *J. Phys. Chem C*, 119, 13799, 2015
 [7] A. Dathe et al., ‘Plasmonic nanoparticles sensors utilizing hybrid modes, electrical excitation, and anisotropic particles’, *Proc. of SPIE* Vol. S. 95500T-1, 2015
 [8] P. Bharadwaj et al., ‘Electrical Excitation of Surface Plasmon’, *PRL* 106, 226802, 3 June 2011
 [9] J. Watanabe et al., ‘Light Emission from Si-Metal-Oxide-Semiconductor Tunnel Junction’, *Jpn. J. App. Phys.* 32,99, 1993
 [10] A. Dathe et al., ‘Electrically Driven Plasmonic Nanoruler’, *Nano Lett.*, 16, 5728, 2016

Tanja Deckert-Gaudig¹, Volker Deckert^{1,2}, V. Pichot³, Denis Spitzer³ // ¹Leibniz Institute of Photonic Technology (IPHT), Albert-Einsteinstr. 9, D-07745 Jena, Germany / ²Institute of Physical Chemistry, Friedrich-Schiller-University Jena and Abbe School of Photonics, Helmholtzweg 4, D-07743 Jena, Germany / ³NS3E «Nanomatériaux pour les Systèmes Sous Sollicitations Extrêmes», UMR ISL/CNRS/UNISTRA, French-German Research Institute of Saint-Louis, 5 rue du Général Cassagnou 68301 Saint-Louis, France

The detonation of microstructured and nanostructured mixtures of TNT (2,4,6-trinitrotoluene) and RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine), commonly known as hexolite, yield nanodiamonds with varying size. Recent works have demonstrated that the detonation of hexolite that was produced via Spray Flash Evaporation (SFE) yields ultra small nanodiamonds with a size of < 4 nm [1,2]. We present a detailed study on TNT-RDX nanocomposites that were obtained in two different approaches with SFE. TNT and RDX were either mixed after separate crystallization (hexolite-1) or the components were already mixed before the crystallization process (hexolite-2). A detailed characterization was performed with conventional Raman and tip-enhanced Raman scattering (TERS) [3,4].

In Figure 1 selected TERS spectra acquired every 5 nm on a hexolite-2 particle are shown. The characteristic highlighted vibrational modes, which are ν_{NO_2} for TNT (red) and the ring breathing for RDX (blue), enable a clear distinction of the components. We will show that the surfaces of the investigated nanoparticles have a TNT content of 80-100 %, while RDX was hardly detected. These results led to the conclusion that hexolite-2 particles were core-shell structures with a RDX core surrounded by a TNT shell.

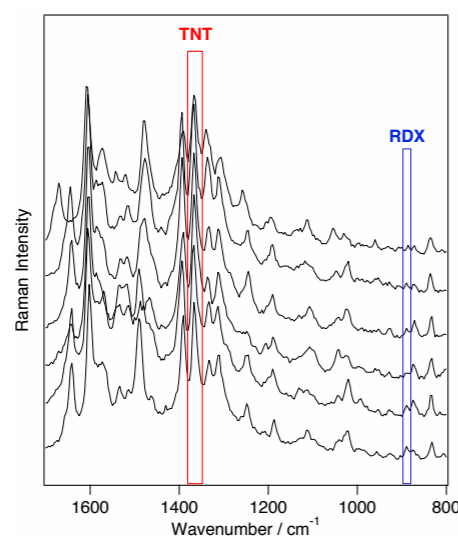


Figure 1 Selected TERS spectra consecutively recorded on a hexolite-2 crystal. The marker bands of TNT and RDX are highlighted red and blue, respectively; step-size between measuring points was 5 nm.

References:

- [1] Risse B., Spitzer D., Hassler D., Preparation of nanoparticles by flash evaporation. Patent, 2013; WO 2013/11767 A1.
- [2] Pichot V., Risse B., Schnell F., Mary J., Spitzer D., Sci. Rep. 3, (2013), 1-6.
- [3] Deckert, V., Deckert-Gaudig, T., Diegel, M., Götz, I., Langedüddecke, L., Schneidewind, H., Sharma, G., Singh, P., Trautmann, S., Zeisberger, M., Zhang, Z. Faraday Discussion 2015; 177: 9-20.
- [4] T. Deckert-Gaudig, V. Pichot, D. Spitzer, V. Deckert, Chem. Phys. Chem. 18, (2017), 175-178.

Vera Dugandžic, Karina Weber, Dana Cialla-May, Jürgen Popp // Leibniz Institute of Photonic Technology, Albert-Einstein-Str. 9, 07745 Jena, Germany / Institute of Physical Chemistry and Abbe Center of Photonics / Friedrich-Schiller University Jena, Helmholtzweg 4, 07743 Jena, Germany

Surface enhanced Raman spectroscopy (SERS) is recognized as a powerful tool for bioanalytical applications, as a consequence of the molecular specificity and high sensitivity it provides. Furthermore, measurements are possible in water solutions, raising the possibility for measurements directly from the body fluids with no or minimal sample preparation. However, there are still many challenges for the SERS application, most of which are associated with nanoparticles used as plasmonic material, leading to poor reproducibility of the measurements. To cope with this problem we developed a strategy for in-situ synthesis of silver nanoparticles in a microfluidic chip, which showed improved short term and long term reproducibility (Fig. 1) compared with measurements performed with batch prepared nanoparticles [1]. This strategy can easily be applied for detection of metabolites from urine and other body fluids. Since biological fluids are complex in terms of their chemical composition, identification of a single analyte by SERS is sometimes very difficult or even impossible. Here, SERS molecular sensors can be applied in order to selectively detect desired analyte from the complex matrix. Herein we present a SERS based molecular sensor for Cu^{2+} ions. The molecular sensor has been synthesized and specificity for Cu^{2+} ions tested against chemically similar ions by means of SERS (Fig. 2). Upon coordination of the Cu^{2+} ion, a shift of the ring breathing mode at 1013 cm^{-1} associated with pyridine is observed (Fig. 2). The intensity of this Raman mode is proportional to the concentration of copper ions. The detection of the Cu^{2+} ions down to $1 \times 10^{-6} \text{ M}$ has been achieved with linearity between 1×10^{-6} and $1 \times 10^{-4} \text{ M}$ (Fig. 3). The proposed SERS molecular sensor for Cu^{2+} ions allowing versatile applications for the monitoring of the trace levels of Cu^{2+} ions.

Financial support from the Federal Ministry of Education and Research, Germany (BMBF) via the projects InfectoGnostics (13GW0096F) and „EXASENS“ (13N13856) is gratefully acknowledged.

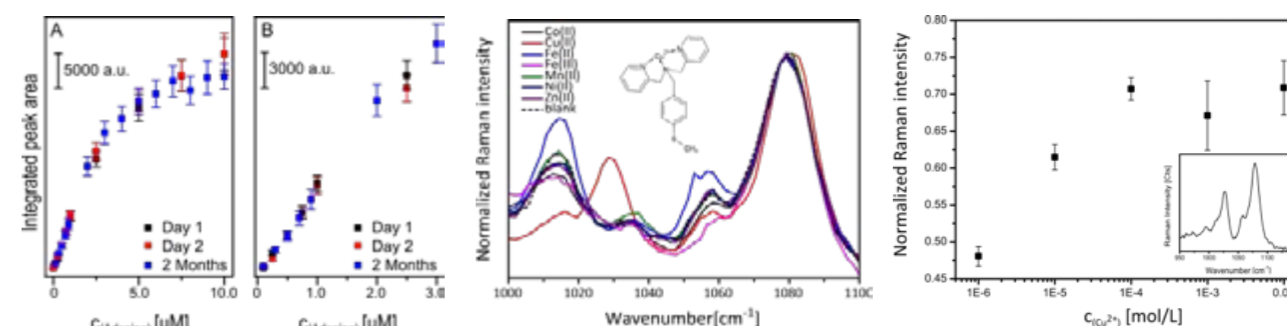


Figure 1: Short and long term reproducibility of the SERS measurements employing in-situ prepared nanoparticles, Figure 2: Specificity of the SERS molecular sensor towards copper(II) ions, Figure 3: Concentration profile for the copper(II) detection using proposed SERS based molecular sensor

References:

- [1] V. Dugandžic et al., Analytica Chimica Acta 946 (2016) 73-79

Betty C. Galarreta, Yulan Hernandez, Luis Ayala // Departamento de Ciencias – Sección Química, Pontificia Universidad Católica del Perú / Av. Universitaria 1801, San Miguel. Lima 32, Peru

Ochratoxin A (OTA) is a secondary metabolite produced by two fungus species, *Aspergillus* and *Penicillium*, that could contaminate many agricultural commodities during harvest and while in storage. Its nephrotoxic, hepatotoxic and carcinogenic effects in humans and animals is a cause of global concern and there is a high demand for methods that are rapid, sensitive and specific [1,2]. Aptamer-functionalized [3] gold nanorods and nanotriangles have been prepared as sensing devices to determine the presence of ppbs of OTA in solution. These nanosensors have been optimized to determine the content of OTA combining two complementary techniques: localized surface plasmon resonance (LSPR) biosensing that monitors the band shifts (Fig.1); and surface-enhanced Raman spectroscopy (SERS) [4] that detects changes in the Raman fingerprint spectra of the adsorbed molecules at the surface of the gold nanostructures (Fig. 2).

This combined detection system could potentially be used in the detection of mycotoxins in food commodities and could be extended to other toxins and molecules of interest in the agricultural industry.

Funding by PNICP (N°132-PNICP-PIAP-2015) and PUCP (PUCP-CAP2015-180) is gratefully acknowledged.

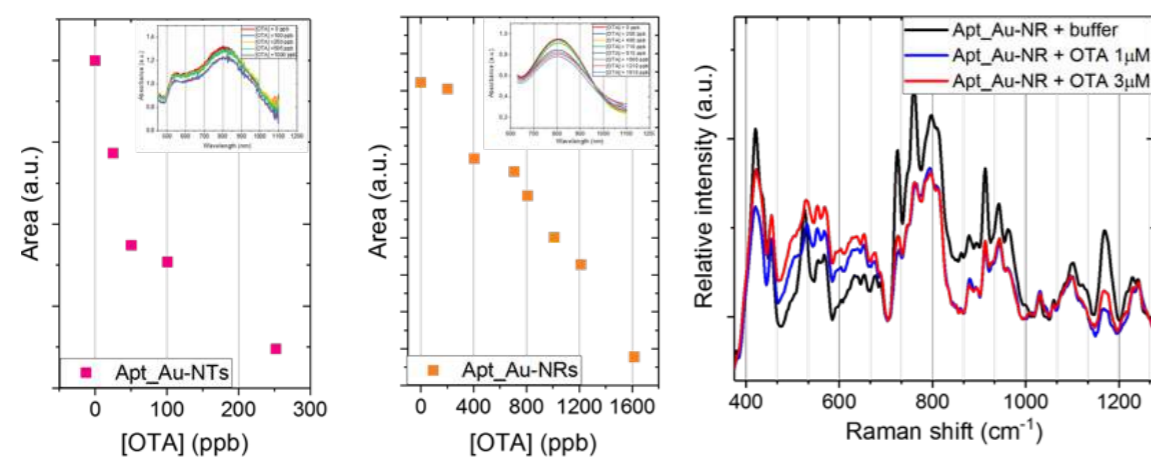


Fig. 1: LSPR analysis of OTA content using gold nanotriangles (Au-NTs) and gold nanorods (Au-NRs) functionalized with aptamer (Apt), Fig. 2: Raman spectra of Apt_Au-NRs at different concentrations of OTA.

References:

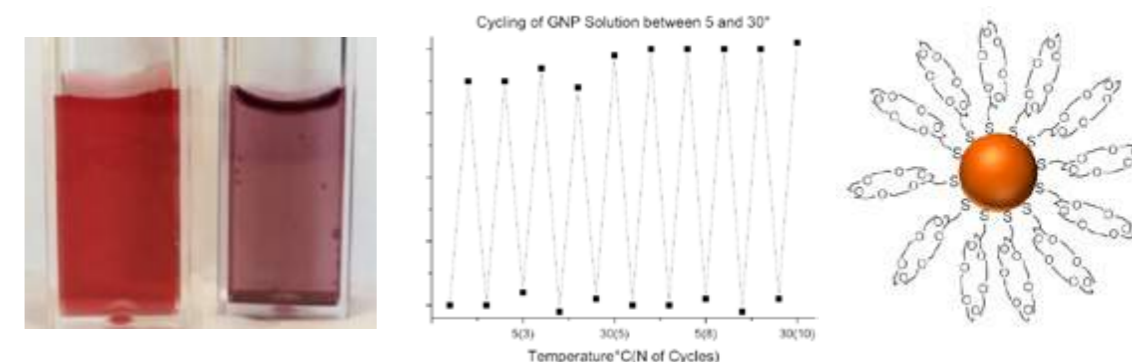
- [1] A. Garcia-Moraleja, et al., Food and Chemical Toxicology 86 (2015) 225-233.
- [2] J.W. Bennett, et al., Clin. Microbiol.Rev. 16 (2003) 497-516.
- [3] J.A. Cruz-Aguado, et al., J.Agric.Food Chem. 56 (2008) 10456-10461.
- [4] B.C. Galarreta et al., Anal.Bioanal.Chem. 405 (2013) 1613-1621.

Mathias Brust and Alex Hill // Department of Chemistry, University of Liverpool, Liverpool L69 7ZD, United Kingdom

The development of gold nanoparticles capable of showing reversible aggregation related to thermo stability has been researched in the past[1, 2], however on all accounts these previous studies have involved large capping agents, typically polymeric systems, which due to their size mask the interaction with the gold surface, hence losing potentially important interactions with the external environment.

Here we present a new thermo-responsive gold nanoparticle system created using simple thiolated crown ethers as capping agents. This new system, both easy to synthesise as well as opening up the gold surface to external interactions, provides a potential new route to more advanced thermo-responsive gold systems. Not only does this system show sensitive thermo-responsive properties, typically seen as a change in colour due to plasmon resonance shifts, but the ability to adhere to a large number of surfaces during its heating phase, forming a water insoluble layer of gold upon the surface in question, a property that could potentially provide new and simple routes to placing mono/multi layers of gold upon a surface.

Not only do these particles show increased interactions with external environments, but show interesting temperature transition changes when subjected to small concentrations (<1mM) of KCl, yet retain their original properties when subjected to LiCl. Distinguishing between alkaline salts like this is a well-known property of crown ethers [3] and integrating gold nanoparticles with highly sensitive salt selectivity could have very useful real world applications.



Funding by the ERC Advanced Grand, project 321172 PANDORA, is gratefully acknowledged.

References:

- [1] X.-Y. Liu, F. Cheng, Y. Liu, W.-G. Li, Y. Chen, H. Pan and H.-J. Liu, Journal of Materials Chemistry, 2010, 20, 278-284.
- [2] R. Iida, H. Mitomo, Y. Matsuo, K. Niikura and K. Ijiro, The Journal of Physical Chemistry C, 2016, 120, 15846-15854.
- [3] S. Blair, E. Kempen and J. Brodbelt, Journal of the American Society for Mass Spectrometry, 1998, 9, 1049-1059.

Daniel Kinzel, Volker Deckert // Leibniz Institute of Photonic Technology, Albert-Einstein-Str. 9, 07745 Jena, Germany, daniel.kinzel@leibniz-ipht.de

Recent near-field Raman spectroscopic measurements based on plasmonic enhancement due to nearby metal nanoparticles show unexpected high lateral resolutions: Tip-Enhanced Raman Scattering (TERS) experiments for instance on protein fibrils [1], single-stranded DNA [2], as well as on porphyrin systems [3] indicate lateral resolutions of less than 1 nm under a wide range of environmental conditions. In order to unravel these resolutions, we aim to describe the underlying effects of plasmon-enhanced Raman scattering processes in a molecule in the vicinity of metal nanoparticles employing theoretical methods such as quantum chemistry and electro-dynamics. In general, the challenge of simulating TERS spectra is the simultaneous description of the electronic structure of the molecule interacting chemically with a nanoparticle (chemical enhancement) and the correct description of the metallic and plasmonic properties of the metal nanoparticle (electromagnetic enhancement).

In particular, chemical interactions between the tip's front-most atom(s) and the surface-anchored analyte molecule(s) can lead to significantly different Raman signatures compared to bulk-averaged measurements, such as normal Raman or even SERS [4]. Implications of the molecular orientation and forced tip-analyte-surface geometries will be discussed in light of the high lateral resolution capabilities of TERS and the selective identification of substances with Raman measurements in general. We will present pure quantum chemical investigations of the local (chemical) effect of metal atoms and clusters, respectively, on the polarizability, and thus on the Raman spectra, of single molecules within a TERS setup. In this contribution, we are going to demonstrate possible sub-nanometer resolution of a sharp TERS tip as a result of chemical interactions, and we will elucidate spectral variations in TERS measurements due to both chemical effects and molecular orientation.

References:

- [1] Deckert-Gaudig, T., Kämmer, E. and Deckert, V. J. Biophotonics 5, 215–219 (2012)
- [2] Lin X, Deckert-Gaudig T, Singh P, Siegmann M, Kupfer S, Zhang Z, Gräfe S, Deckert D, arXiv:1604.06598 (2016)
- [3] Zhang, R. et al. Nature 498, 82–86 (2013).
- [4] Latorre F, Kupfer S, Bocklitz T, Kinzel D, Trautmann S, Gräfe S, Deckert V, Nanoscale 8, 10229-10239 (2016)

F. Madzharova, Z. Heiner¹ and J. Kneipp // Department of Chemistry, Humboldt-Universität zu Berlin, Brook-Taylor-Str. 2, 12489 Berlin, Germany / ¹School of Analytical Sciences Adlershof SALSA, Humboldt-Universität zu Berlin, Albert-Einstein-Str. 5-11, 12489 Berlin, Germany

In the local optical fields of plasmonic nanostructures, many vibrational spectroscopic effects such as the incoherent, spontaneous Raman scattering or its nonlinear analogue hyper-Raman scattering can benefit from strong surface enhancement. Surface-enhanced hyper-Raman scattering (SEHRS) follows different selection rules and different enhancement mechanism compared to surface-enhanced Raman scattering (SERS), and thus it can provide complementary chemical and structural information about the molecule-nanostructure system under investigation. Additionally, SEHRS can be more sensitive than SERS with respect to local environment and orientation of the probed molecules on the metal surface [1, 2]. In particular, combined SEHRS/SERS approaches can provide new insights into interactions of plasmonic metal nanoparticles with small bio molecules, which are the building blocks of cells and tissues [2, 3].

Here, we present non-resonant SEHRS spectra of nucleic acid bases and aromatic amino acids at 1064 nm excitation. We compare the data with SERS spectra at 532 nm and discuss the observed variations in relative signal strengths of many molecular vibrations in terms of the different selection rules for the one- and two-photon excited Raman process. In addition, we compare the SERS and SEHRS enhancements in the local optical fields of different silver nanoaggregates and for different biomolecules. In particular, we investigated the influence of variation in pH and molecule concentration on the SEHRS and SERS spectra. The results support the high sensitivity of SEHRS spectra with respect to small environmental changes, and strongly suggest SEHRS as a tool to probe biomolecule-nanoparticle interactions.

Financial support from FCI (Chemiefonds Fellowship), ERC (Grant No. 259432), and DFG GSC 1013 (SALSA) is gratefully acknowledged.

References:

- [1] J. C. Hulteen et al., Langmuir 22 (2006) 10354-10364.
- [2] F. Madzharova et al., The Journal of Physical Chemistry C 121 (2017) 1235-1242.
- [3] F. Madzharova et al., The Journal of Physical Chemistry C 120 (2016) 15415-15423.

Robert Meyer^{1,2}, Steffen Trautmann^{1,2}, Volker Deckert^{1,2} // ¹Institute of Photonic Technology, Albert-Einstein-Str. 9, 07745 Jena, Germany / ²Institute of Physical Chemistry & Abbe Center of Photonics, Friedrich-Schiller-University Jena, Lessingstraße 10, 07743 Jena, Germany

Photoinduced force microscopy (PiFM) is a novel optical near field technique based on the optical excitation of a sample and detecting the resulting photoinduced force between tip and sample. Since the magnitude of this force depends on the photo-induced molecular polarizability in the sample, PiFM reveals spectroscopic sensitivity. As the photo-induced forces are spatially confined on the nanometer scale, high spatial resolution (<10 nm) in ambient conditions can be obtained.[1] The imaging properties of PiFM have been recently demonstrated by mapping the electrical field distributions of conventional AFM cantilever probes.[2] Here, we map the field distribution with nanometer resolution of silver evaporated AFM tips (TERS Tips), with respect to the incident wavelength according to the plasmon resonance of the TERS tip (Fig. 1). The measurements were performed on a glass substrate by direct detection of the optical forces between the TERS tip and its induced image dipole. Since the efficiency of the tip-enhancement is polarization dependent [3], radial polarized light will generate the highest enhancement at the TERS tip. Consequently, different incident polarization states (linear, azimuthal, radial) are characterized by PiFM. The experimental results for conventional AFM tips are in good agreement with theoretical models (Fig. 2) and thus empower predictions towards field distributions of TERS tips.

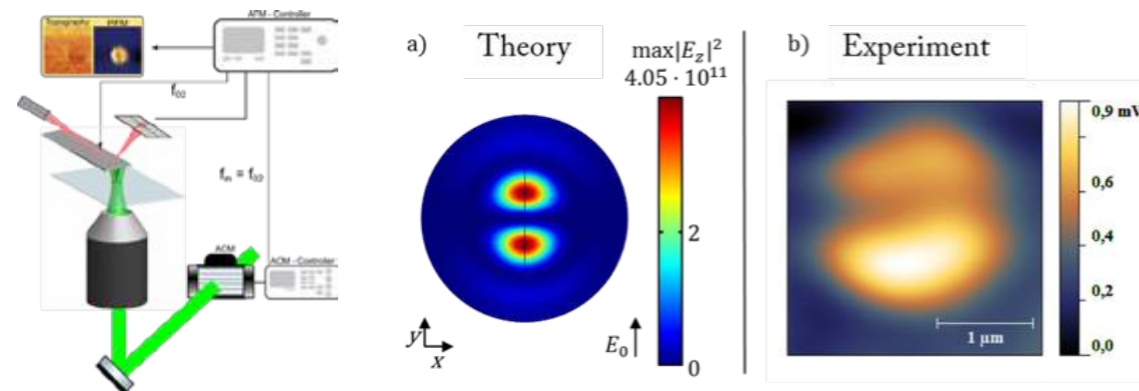


Fig. 1: Setup for PiFM, Fig. 2: a) Theoretical calculations of the electromagnetic field distribution for a conventional AFM tip for linear polarized light. b) Experimental result in good agreement with theory.

References:

- [1] J. Jahng et al., Acc. Chem. Res., 48 10 (2015) 2671–2679.
- [2] F. Huang et al., Sci. Rep.,5 (2015) 10610.
- [3] Y. Saito et al., Chem. Phys. Lett., 410 1–3 (2005) 136–141.

Clyde Midelet¹, Bruno Le Pioufle², Olivier François³, Martinus H.V. Werts¹ // ¹SATIE, École normale supérieure de Rennes, CNRS, campus de Ker Lann, F-35170 Bruz, France, ²SATIE, Ecole normale supérieure Paris-Saclay, F-94235 Cachan, France, ³ESIEE-Paris, ESYCOM, University Paris-Est, F-93160 Noisy Le Grand, France.

In a simple, homogeneous, isotropic, liquid environment in the absence of external fields, the motion of nanoparticles is directed by Brownian forces leading to a random perpetual motion of the individual particles. A sufficiently strong force is needed to overcome the Brownian motion and to control the motion of the particles. Metal nanoparticles in solution present an electric double layer (the “ion cloud”) around these particles, which renders them polarizable and permits the use of an electric field gradient to control the motion of the particles via the dielectrophoretic force. This force is given by:[1]

$$F_{DEP} = 2\pi R^3 \epsilon_m \epsilon_m K_{CM} \nabla E_{RMS}^2$$

There are three factors that influence the dielectrophoretic force: the electric field (frequency, amplitude, 3D topology), the particles (size, shape, composition) and the suspending liquid (polarizability, ionic strength, pH).

In combination with optical and spectroscopic measurements these parameters may be exploited for quantifying the interactions at the surface of plasmonic nanoparticles and biomolecules.[2] This is of interest for developing biosensing schemes.

Here, we report on functionalized gold nanoparticles tracked directly inside microfluidic channel by dark-field video microscopy, using the strong plasmonic light scattering response of gold nanoparticles.[3] Transparent micro-electrodes (ITO) are used to apply a high-gradient AC electric field.

Using computer control, we are able to synchronize the switching of the electric field and the video acquisition permitting the analysis of the dielectrophoretic trapping and also the diffusion coefficient, opening up new possibilities for the characterization of simple and more complex nanoparticles samples.

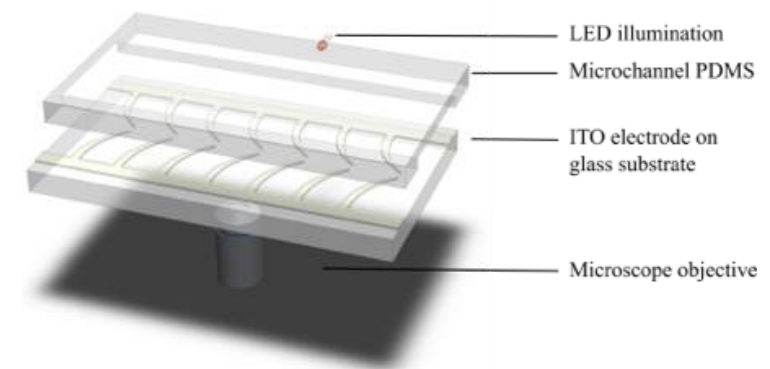


Fig. 1: Schematic representation of a transparent microfluidic device with LEDs for dark field illumination. Scattered light, as well as fluorescence can be observed through the glass electrode substrate using a microscope objective.

References:

- [1] T. Jones, “Basic theory of dielectrophoresis and electrorotation,” IEEE Eng. Med. Biol. Mag., no. December, pp. 33–42, 2003.
- [2] H. Morgan and N. G. Green, AC Electrokinetics: colloids and nanoparticles. Baldock, England: Research Studies Press Ltd., 2003.
- [3] C. Midelet et al., “Effects of biomolecules on the electrokinetics of colloidal nanoparticles in liquid suspension,” Proc.SPIE, vol. 10078, p. 100780T, 2017.

Heike L.K.S. Mosch, Frank Garwe¹, Robert Müller^a, Wolfgang Fritzsche¹, Thomas Krech², Thomas Rainer³, Achim Stolle // Institute of Technical Chemistry and Environmental Chemistry, Friedrich-Schiller-University Jena, Lessingstraße 12, 07743, Germany / ¹Leibniz Institute of Photonic Technology, Albert-Einstein-Str. 9, 07745 Jena, Germany / ²JENOPTIK I Automotive, JENOPTIK Automatisierungstechnik GmbH, Konrad-Zuse-Straße 6, 07745 Jena, Germany / ³boraident GmbH, Köthener Straße 33A, 06118 Halle (Saale), Germany

Plasmons in activated metal nanoparticles are capable of initiating reactions of atoms or molecules located on the particle surface.[1] Like this, oxidation,[2] reduction[3] or even degradation of compounds could be observed. [1,4] In our research, we seek to make use of the plasmonic effect in gold nanoparticles for heterogeneous catalysis in gas phase to degrade volatile monoterpenoids as model contaminants to smaller molecules, ideally CO₂, in presence of air as oxidizing agent.

As catalyst, gold nanoparticles are used on a porous glass support (Fig. 1, left). Being placed in the reactor of the testing plant (Fig. 1, at center), the catalyst is permanently activated by the illumination with a Xe arc-lamp with 300 W power and a spectrum of 200-900 nm. The model contaminant, here 3-methyl-2-butenal (prenal) in gas phase (carrier gas N₂ and air as oxidant) can then be degraded in continuous flow. The products of the catalysis reaction are monitored by an online gas chromatograph equipped with a flame ionization and a thermal conductivity detector. In experiments, the contaminant concentration was varied and promising results were obtained for flow rates of V=50 mlmin⁻¹ and 100 mlmin⁻¹, as degradation rates of maximum 60 % of the initial concentration could be achieved (Fig. 1, right). Higher flow rates are however problematic. Although high flow rates are challenging, the plasmonic effect can therefore be regarded as very interesting tool for heterogeneous catalysis of contaminants in gas phase.

We thank pades Partikeldesign Thüringen and the BMBF for the funding of this project.

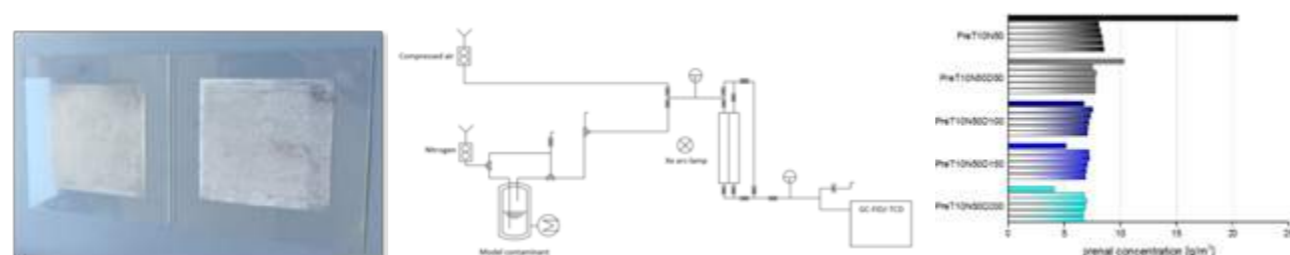


Fig. 1: Catalyst AuNPs on porous glass support (left), setup of catalysis testing plant (at center), degradation results of model contaminant prenal at different volume flows (nitrogen / compressed air) with a saturator temperature of 10 °C (right).

References:

- [1] S. Mukherjee et al., Nano Lett. 2013, 13, 240 - 247.
- [2] P. Christopher, H. Xin, S. Linic, Nat. Chem. 2011, 3, 467 - 472.
- [3] T. Wu et al., Nanoscale 2011, 3, 2142 - 2144. [4] X. Zhou et al., J. Phys. Chem. C 2010, 114, 2746 - 2750.

Rafał Nowaczynski, Piotr Paszke, Andrea Csáki², Paweł Osewski¹, Marcin Gajc¹, Dorota Anna Pawlak¹ // Centre of New Technologies, University of Warsaw, S. Banacha 2c Str., 02-097 Warsaw, Poland / ¹Institute of Electronic Materials Technology, Wólczynska 133 Str., 01-919 Warsaw, Poland / ²Institute of Photonic Technology, Albert-Einstein-Str. 9, 07745 Jena, Germany

In this work we are obtaining Whispering Gallery Mode (WGM) resonators in a form of glass microspheres. This kind of structures are capable of detecting small amount of particles attached to their surface, making them a perfect tool in biological sensor applications [1]. Additionally, embedding quantum dots (QDs) and metallic plasmonic nanoparticles in the spherical optical cavity enables achieving much greater Q-factor and sensitivity than that of a pure glass resonators [2]. The glass doping is realized using NanoParticle Direct Doping (NPDD) [3] method with CdTe QDs and silver nanoparticles. After doping, glass is grinded to fine powder and processed in a free-fall furnace to produce microspheres (Fig. 1). Three different glasses were evaluated to be used as the material matrix: sodium borophosphate glass (NBP), sodium aluminophosphate glass (NAP) and tellurite glass (TZN). Microspheres made of each were functionalized with GOPS silane and fluorescent A₃NF oligonucleotide to determine their usability as biological sensors [4]. While NBP showed surface degradation (Fig. 2), NAP and TZN were successfully functionalized without destructive changes to their surface (Fig. 3), making them good candidates for biological sensors in WGM-based resonator systems.

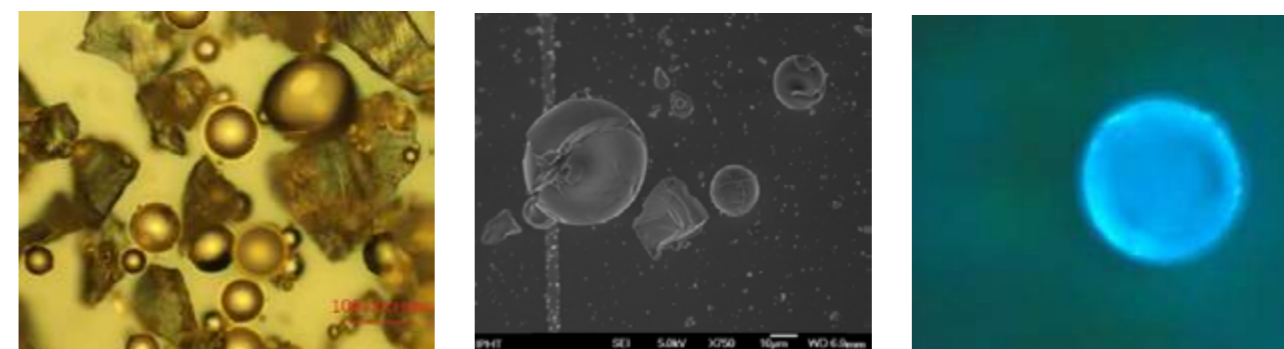


Fig. 1: Microspheres obtained from a powdered, quantum dot doped glass using the free-fall furnace, Fig. 2: Surface degradation of NBP glass microspheres after functionalization, Fig. 3: Fluorescence of A₃NF on functionalized NAP glass microsphere

References:

- [1] Vollmer, F. et al. Proc. Natl. Acad. Sci. U. S. A., 2008, 105,52, 20701-20704.
- [2] Yang, J.; Guo, L. J. IEEE J. Sel. Topics Quantum Electron. 2006, 12,1, 143-147.
- [3] Gajc, M.; Pawlak, D. A. et al. Adv. Funct. Mat. 2013, 23, 3443.
- [4] Möller, R.; Csaki, A.; Köhler, J. M.; Fritzsche, W. Nucleic Acids Research 2000, 28, (20e91).

Piotr Paszke, Paweł Osewski¹, Rafał Nowaczynski, Dorota Anna Pawlak // Centre of New Technologies University of Warsaw, 2c Banacha Str., 02-097 Warsaw, Poland / ¹Institute of Electronic Materials Technology, 133 Wólczynska Str., 01-919 Warsaw, Poland

In this work we present a system for exciting a WGM (whispering gallery mode) microresonators. WGM microresonator is a type of optical resonator in which light is trapped in round trip by total internal reflection. There are many various designs including microdisks, microtoroids, and dielectric microspheres [1]. Whispering gallery mode (WGM) can be utilized for many applications, for example as narrow band lasers or thermo- and biosensors. Several coupling methods of WGM have been reported, such as prism coupling, tapered fiber, integrated waveguide, and angle polished fiber [2].

Our system for exciting WGM microresonators use method with tapered fiber coupling, because this method let us measure WGM resonances in very simple way, as dips in transmission of light through the tapered fiber in a function of wavelength. Our system contains a supercontinuum light source, a monochromator with high resolution for obtaining very narrow and continuously tunable light which is modulated and introduced to tapered waveguide. The light is coupled into the WGM microresonator using evanescent wave from the tapered waveguide. Changes in a transmission intensity are registered using a photodiode connected to lock-in amplifier. Program on PC connected with the monochromator and lock-in amplifier is drawing the plot of transmission in a function of wavelength.

References:

- [1] Yuze Sun; Xudong Fan, Anal Bioanal Chem 2011, 399, 205–211.
[2] J. Ward, O. Benson., Laser Photon. Rev 5, Issue 4, July 2011, 553–570

Victor K. Pustovalov, Liudmila G. Astafyeva¹, Wolfgang Fritzsche² // Belarusian National Technical University, Nezavisimosti pr. 65, Minsk, 220013, Belarus / ¹B.I. Stepanov Institute of Physics, National Academy of Sciences of Belarus, Nezavisimosti pr. 68, 220072, Minsk, Belarus / ²Leibniz Institute of Photonic Technology, Jena, A. Einstein Str. 9, 07745, Germany

The investigations and the use of nanoparticles as photothermal agents in solar and photonic nanotechnology represent a fast growing area of research and applications. Potential benefits include the possibility for the applications of nanoparticles for absorption of solar radiation, a light-to-heat conversion, for applications in nanoenergy, solar cells, photocatalysis, etc. The efficiency of applications of metallic nanoparticles for solar and photo-thermal nanotechnology depends on plasmonic properties of nanoparticles, characteristics of radiation and surrounding medium, etc. Efficiency factors of absorption K_{abs} and scattering K_{sca} of optical radiation with wavelength λ by spherical NP with radius r_0 are calculated based on Mie theory [1]. The normalized refractive index of particles was used in Mie theory because NPs are immersed in water. The parameter $P1 = K_{abs} / K_{sca}$ describes the correlation between absorption and scattering of radiation by NP and characterizes the contribution of the absorption process. The parameter $P1$ can be used for determination of the NP types predominantly as an absorbers of radiation for $P1 > 1$. The results of comparative analysis of the plasmonic properties of metallic nanoparticles allow to select their parameters for effective nanosolar and nanophotonic applications.

Optical properties of several metallic (aurum, platinum, zinc, nickel, titanium, silver, molybdenum, and palladium) nanoparticles are theoretically investigated in the spectral interval 200-2500 nm and the analysis of them has been carried out. The investigation of the influence of nanoparticle parameters (type of metal, their radii, optical indexes, etc.), on optical properties of nanoparticles has been conducted. The selection of appropriate properties of NPs is based on the choice of the NP metal and radius with $K_{abs}(\lambda)$ of metallic NPs for overlapping the spectral dependence of solar irradiance $IS(\lambda)$ and the choice of the parameter value $P1 \geq 1$ for whole interval 200-2500 nm. It was established, that spherical titanium, nickel, molybdenum, and palladium nanoparticles with the radii of about 75 nm can be applied for effective absorption of solar radiation and following heating of nanoparticles.

The strongly enhanced absorption of spherical metallic NPs makes them a novel and highly effective class of contrast agents for solar nanoenergetic and PT applications for absorption of solar radiation with continuous spectrum in a wide spectral interval of 200-2500 nm.

References:

- [1] Bohren, C.F., Huffman, D.R., 1983. Absorption and Scattering of Light by Small Particles. Wiley, New York

Ludovic Roussille¹, Annika Franke², Selene Mogavero, Bernhard Hube², and Volker Deckert¹ // ¹Leibniz Institute of Photonic Technology (IPHT), Albert-Einstein-Str. 9, 07745 Jena, Germany / Institute of Physical Chemistry and Abbe center of Photonics, Friedrich Schiller University Lessingstrasse 10, 07743 Jena, Germany / ²Department Microbial Pathogenicity Mechanisms, Leibniz Institute for Natural Product Research and Infection Biology (HKI), Beutenbergstrasse 11a, 07745 Jena Germany

How to localize a protein on a cell membrane?

Cell membranes incorporate many proteins of different size. In order to directly differentiate between different proteins, the molecule of interest is usually specifically labeled. However, if the protein is only a small peptide, like the *Candida albicans* peptide-toxin Candidalysin which is only 31 amino acids long [1], any molecule or nanoparticle used to label the peptide will substantially increase its size. Consequently it might deeply affect the actual peptide function.

AFM-TERS is based on the creation of a local plasmon at the apex of a scanning microscopy tip, which leads to an enhanced Raman signal. While it is challenging to discriminate between different proteins directly, Raman spectroscopy is very sensitive to the change of a hydrogen by a deuterium. Hence, deuteration is a promising alternative to label such a small peptide and maintain its function.

Candidalysin is a peptide secreted by *C. albicans*, which has been shown to be responsible for host cells damage. However, the respective mechanism remains unclear. Therefore, nanometer scale localization of the peptide, and potential simultaneous structural change determination, will be essential to gain a better understanding of the actual mechanism. Our data show first TERS measurements that potentially allow such a high resolution analysis. We were able to detect the presence of deuterated Candidalysin by AFM-TERS on cells, which directly implies the presence of the peptide in/on the cell membrane.

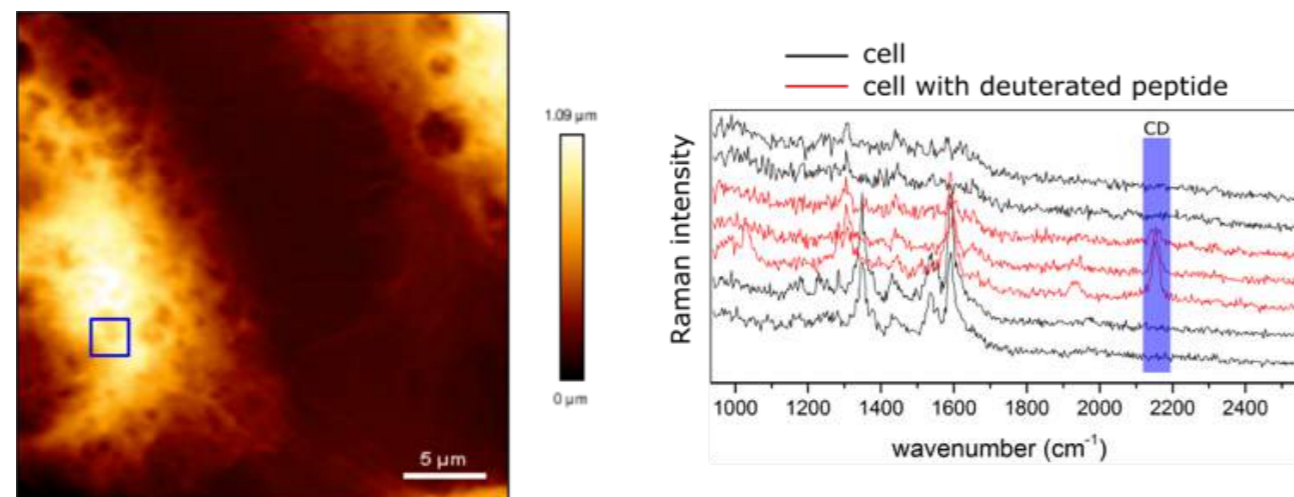


Fig1: AFM image of an epithelial cell destroyed by incubation with deuterated Candidalysin.

References:

[1] Moyes et al, Nature 532 (2016) 64-68

Janne Simonen, Joakim Linja, Jussi Toppari // University of Jyväskylä, Department of Physics, Nanoscience Center, P.O. Box 35, 40014 University of Jyväskylä, Finland

Metal nanoparticles have localized plasmon resonances that can be excited by incident light. The exact wavelength of the resonance depends on the size and shape of the nanoparticle. The resonances are usually dipolar in nature, and radiate predominantly into the substrate on which the particles are placed, making them interesting for waveguide coupling applications.

Continuing our earlier studies of metal nanodiscs as waveguide couplers [1], we investigated the properties of random arrays of tilted metal nanocones for coupling incident light into propagating modes within the substrate. We will present theoretical and experimental results for the coupling efficiency for a range of nanocone metasurfaces of different dimensions and tilt angles, especially in view of using them as directional waveguide couplers.

For the experiments, we fabricated gold nanocone metasurfaces on glass substrates by hole mask colloidal lithography, and measured the intensity of light emitted from the edges of the waveguides at normal illumination through a monochromator.

For simulations, we employed the finite element method (Comsol Multiphysics), studying the coupling efficiency of a single nanocone. We evaluated the accuracy of various 2D and 3D schemes and found that while some insight can be extracted from less computationally intensive 2D and small 3D models, a 3D simulation domain of several wavelengths in size is required to reach accurate results, especially concerning the radiation patterns of light scattered by the nanocones. This is due to the strong near-field effects exhibited by the plasmonic nanoparticles.

Funding by the EU INNO INDIGO project Window Integrated Solar Collector is gratefully acknowledged.

References:

[1] A. Pennanen and J. Toppari, Opt. Express, vol. 21 Suppl 1, no S1, pp. A23-35 (2013).

Chandan Singh^{1,2}, Sophie Thamm¹, Matthias Thiele¹, Andrea Csáki¹, Thomas Henkel¹, Ondrej Stranik¹, Gajjala Sumana², Wolfgang Fritzsche¹ // ¹Institute of Photonic Technology, Albert-Einstein-Str. 9, 07745 Jena, Germany / ²CSIR National Physical Laboratory, New Delhi, India 110012.

In this work a route for the immobilization of cetyl trimethyl ammonium chloride capped gold nanocubes (CTAC-AuNCs) on glass surfaces is demonstrated for Localized Surface Plasmon Resonance (LSPR) based bio-sensing application. The synthesis of CTAC-AuNCs has been achieved by using a seed mediated growth with a microfluidic platform [1]. The surfactant (CTAC) has been extracted using trichloromethane (CHCl₃) followed by the ligand exchange procedure for colloidal AuNCs solution using Poly(sodium 4-styrenesulfonate)(PSS) and trisodium citrate (TSC) [Fig.I][2]. Afterwards AuNCs were immobilized on amine modified glass chip. The chip was integrated into a chamber that is connected to a microfluidic setup and enables therefore the injection of different glucose concentrations to alter the refractive index. As shown in Fig.II, AuNCs have displayed a significant shift of the LSPR peak position with respect to the change in refractive index of the surrounding medium. Further, immobilization of capture DNA on AuNCs followed by the subsequent binding of *Aspergillus* target DNA has been performed. This is demonstrated by the corresponding changes in the absorption peak, initially due to the binding of capture DNA and then following its successful hybridization with target DNA (Fig.III).

Financial support from DAAD is gratefully acknowledged.

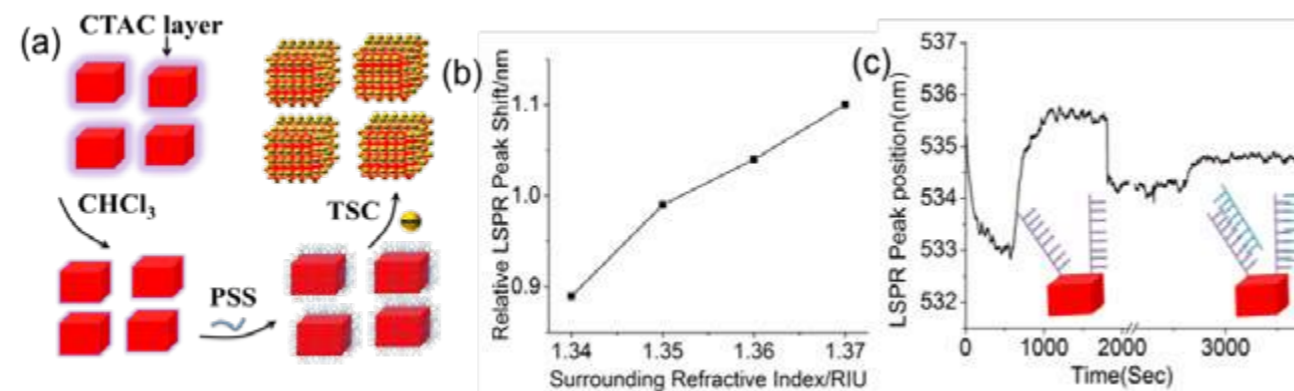


Fig.I: Schematic representation of designing citrate capped AuNCs, Fig.II: Shift in the LSPR peaks with respect to change in the surrounding medium refractive index., Fig.III: Response curve for binding of probe DNA and target DNA on AuNCs.

References:

- [1] M.Thiele et al. Lab Chip, 17(2017)1487-1495
 [2] J. G. Mehtala et al. Langmuir, 30(2014)13727-13730

Egor Kaniukov¹, Olga Zukovskaja^{2,3,4}, Karina Weber^{2,3,4}, Dzmitry Yakimchuk¹, Dana Ciiala-May^{2,3,4}, Steffen Teichert⁵, Arne Bochmann⁵, Jürgen Popp^{2,3,4}, Liubov Osminkina⁶, and Vladimir Sivakov² // ¹Cryogenic Research Division, Scientific-Practical Materials Research Centre NAS of Belarus, P. Brovki Str. 19, 220072 Minsk, Belarus / ²Leibniz Institute of Photonic Technology Jena, Albert-Einstein-Str. 9, 07745 Jena, Germany / ³Friedrich Schiller University Jena, Institute of Physical Chemistry and Abbe Center of Photonics, Helmholtzweg 4, 07745 Jena, Germany / ⁴Research Campus Infectogistic, Philosophenweg 7, 07743 Jena, Germany, Germany / ⁵Ernst-Abbe-Hochschule Jena, Carl-Zeiss-Promenade 2, 07745 Jena, Germany / ⁶Lomonosov Moscow State University, A.N. Belozersky Institute of Physico-Chemical Biology, Leninskie Gory 1, 119991 Moscow, Russian Federation.

It is very interesting and challenging to understand the formation mechanism of plasmonic nanostructures array with even more complex, but adjustable structures using simpler routes under mild conditions and investigates in details the kinetic of self-organization processes of silver, copper and gold nanostructures in limited volumes (pores). The targeted scientific breakthrough is a study of controlled self-organized process of nanosized structures based on porous silica on silicon surface systems where dielectric pores are selectively filled by noble metals (silver, copper and gold) for a formation of dimensionally divided plasmonic nanostructures. Swift heavy ion track technology has been applied for the pre-patterning of porous surfaces with nanoscaled metal nanoparticles. Wet-chemical methods of the deposition of noble metals and their combinations in the pores have been applied for the formation of the plasmonic nanostructures and will be discussed in details. The characterization of plasmonic structures were carried out by surface analytic methods like SEM, EDX, EBSD, TEM, etc., which are combined with theoretical modeling of growth processes and plasmonic properties supporting the optimization process of the surface.

Funding by BMBF(01DS14017), DAAD program and MOST Horizon-2020 is gratefully acknowledged.

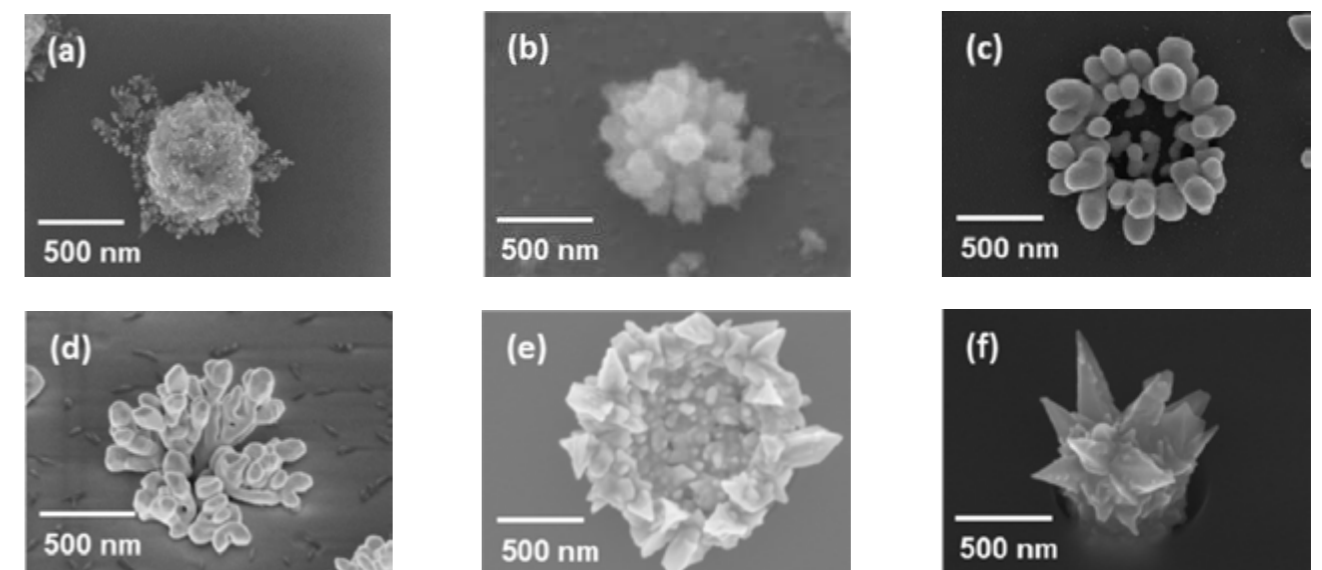


Fig. 1. Scanning electron microscopy micrographs of self – organized copper (a, b), silver (c, d), and gold (e, f) nanostructures grown in porous Si/SiO_x matrix.

References:

- [1] V. Sivakov et al., J. Crystal Growth 400, 21-26 (2014).
 [2] E. Kaniukov et al., Nanotechnology 27 (11), 115305 (2016).

Gergo Peter Szekeres, Vesna Zivanovic, Daniela Drescher, Tina Büchner, Janina Kneipp // Humboldt-Universität zu Berlin, Department of Chemistry, Brook-Taylor-Str. 2, 12489, Berlin, Germany

When a nanoparticle is introduced into a biological system, such as a cell, biomolecules surround it immediately, forming a so-called biomolecule- or protein corona. This corona determines the path of the nanoparticle inside the cell, as this is what the cell 'sees' [1]. One of the most promising methods in the investigation of the accumulation and the formed protein corona of nanoparticles is surface-enhanced Raman scattering (SERS) mapping, when plasmonic nanoparticles are applied in the incubation experiments [2].

In this study, plasmonic nanoparticles of different shape, size, and surface functionalization have been introduced to protein solutions and different cell lines, which then were incubated for a range of different time intervals. After the incubation, SERS spectra were collected. Useful information could be extracted about the accumulation sites of the nanoparticles from the integrated Raman intensity maps, and the spectra directly indicate the biochemical surrounding of the nanoparticles, referring to the protein corona itself.

Funding by DFG GSC 1013 School of Analytical Sciences Adlershof (SALSA) and ERC grant 259432 to J.K. is gratefully acknowledged.

References:

- [1] D. Walczyk et al., *J. Am. Chem. Soc.*, 132 (2010), 5761–5768.
- [2] D. Drescher and J. Kneipp, *Chem. Soc. Rev.*, 41 (2012), 5780-5799. D. Drescher et al. *Nanoscale*, 5 (2013), 9193-9198. Drescher et al. *Adv. Funct. Mater.* 24 (2014), 3765-3775. T. Büchner et al., *Analyst*, 141 (2016), 5096-5106.

Sophie Thamm, André Dathe, Janina Wirth, David Zopf, Andrea Csáki, Wolfgang Fritzsche // Leibniz Institute of Photonic Technologies, Albert-Einstein-Str. 9, 07745 Jena, Germany

Optical spectroscopy of metallic structures which support localized surface plasmon resonances (LSPR) can be used for DNA detection. The method represents a label-free approach, with rather high sensitivity in comparison to other label-free techniques. By an external, incident light beam, density oscillations of the nanoparticle conduction electrons are induced at a specific wavelength. This occurring resonance band is sensitive to changes of the surrounding medium, which gives the opportunity to utilize them as label-free bioanalytical sensors [1]. Biomolecules, here DNA, bind directly on the gold nanoparticle's surface which leads to a change of the local refractive index and results in a shift of the peak wavelength (Fig. 1) [2,3]. This effect points at the presence of biomolecules in our solution. Establishing this DNA detection method for a plasmonic microarray [4] is the aim. Further studies have shown the potential to use the interaction between laser pulses, DNA and silver nanoparticles (Ag-NPs) for biomanipulation [5]. In this case Ag-NPs are coupled to the DNA and an excitation transfer is detectable after femtosecond laser irradiation. The escape of electrons and their transfer is of high interest for bottom-up techniques regarding nanoelectronic devices. Here we show the potential to combine these studies with AFM-based nanomanipulation in order to characterize the excitation transfer in DNA and their superstructures (Fig. 2).

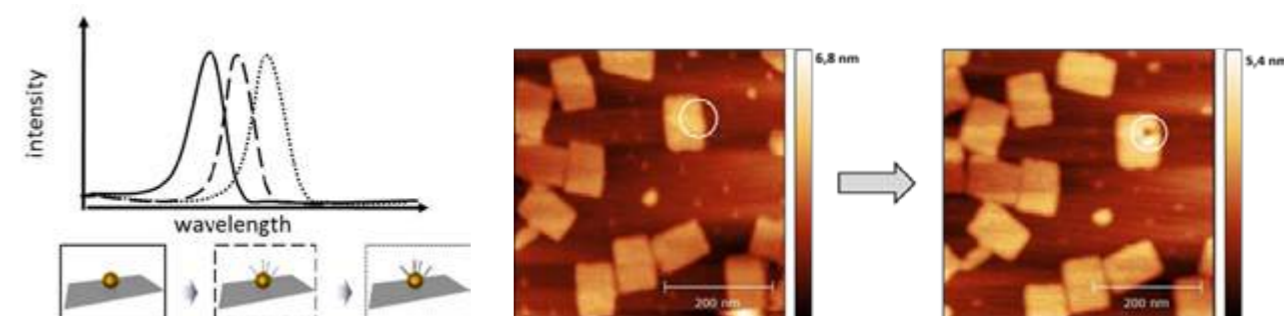


Fig. 1: The adsorption of the thiol-capture DNA and the hybridization with the target DNA leads to a shift in the LSPR specific wavelength, Fig. 2: Nanomanipulation by free positioning of the AFM tip (Software: Nanoman by Bruker). The DNA-Origami is shown before (left) and after (right) the precise local manipulation.

References:

- [1] U. Kreibig and M. Vollmer, *Optical Properties of Metal Clusters*, Springer, Berlin, 1995.
- [2] T. Schneider, N. Jahr, J. Jatschka, A. Csaki, O. Stranik and W. Fritzsche, *Journal of Nanoparticle Research*, 2013, 15, 1-10
- [3] Jatschka, J. Propagating and localized surface plasmon resonance sensing – A critical comparison based on measurements and theory, *Sensing and Bio-Sensing Research*, 2016, 7, 62-70
- [4] Zopf, D.; et al. Hyperspectral imaging of plasmon resonances in metallic nanoparticles. *Biosensors and Bioelectronics* 2016, 81, 287-293
- [5] Wirth, J Plasmonic Nanofabrication by Long-Range Excitation Transfer via DNA Nanowire. *American Chemical Society* 2011

Steffen Trautmann¹, Volker Deckert^{1,2,3} // ¹Institute of Physical Chemistry, University of Jena, Helmholtzweg 4, 07745 Jena, Germany / ²Leibniz Institute of Photonic Technology, Albert-Einstein-Str. 9, 07745 Jena, Germany / ³Abbe Center of Photonics, University of Jena, Albert-Einstein-Str. 6 D-07745 Jena, Germany

Tip-enhanced Raman Spectroscopy (TERS) provides chemical information with subnanometer resolution. However, from a practical point of view, it is difficult to get a detailed mapping of molecules in the nanometer range due to the intrinsic and unavoidable thermal drift of the system and the generally long acquisition times of CCD based Raman systems.

Here we developed a new system that records a bandwidth selected spectral response synchronously to the AFM imaging in order to create rapid and precise tip-enhanced Raman maps (Fig. 1). Specifically, we demonstrate the potential to acquire tip-enhanced Raman signals (by integration of the signal of a large spectral range using a balanced photoreceiver) for one pixel within an acquisition time of 4 ms.

Figure 2 shows domains of Raman active molecules (DNA origami) what can be visualized during the AFM measurement. It is our belief that this method enables an easier correlation of AFM and TERS information and consequently locates molecules on various substrates and effectively overcomes the thermal drift problem. This way AFM-based TERS set up, can reach resolutions similar to STM considering chemical effects.[1]

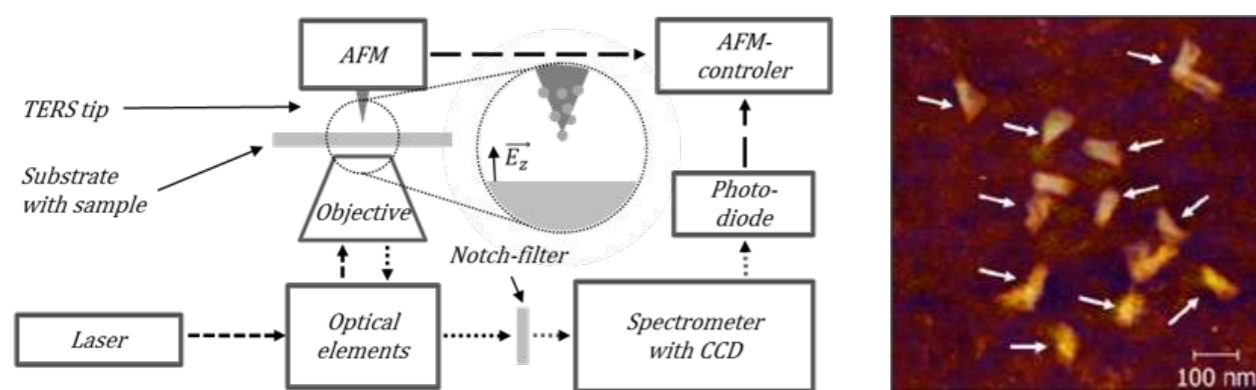


Fig. 1: schematic from the experimental iTERS setup, Fig. 2: iTERS image (height+diode signal) from Origamis on glass. Yellow areas Origamis with active tip. Signal loss was at half-finished image.

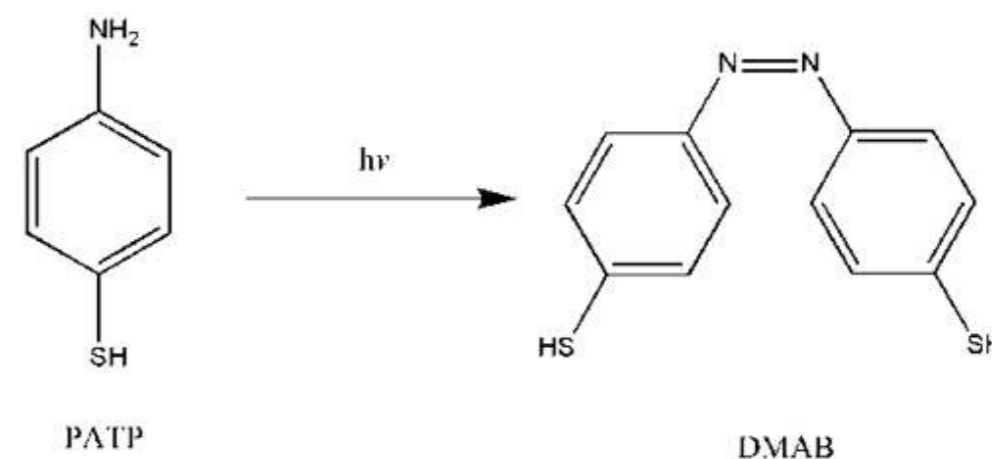
References:

- [1] F. Latorre, S. Kupfer, T. Bocklitz, D. Kinzel, S. Trautmann, S. Gräfe, and V. Deckert, "Spatial resolution of tip-enhanced Raman spectroscopy – DFT assessment of the chemical effect," *Nanoscale*, vol. 8, no. 19, pp. 10229–10239, 2016.

Zhiyang Zhang^{1,2}, Virginia Merk¹, Ulrich Panne^{1,2}, Merwe Burman², and Janina Kneipp^{1,2} // ¹Humboldt-Universität zu Berlin, School of Analytical Sciences Adlershof and Department of Chemistry, Brook-Taylor-Str. 2, 12489 Berlin, Germany / ²BAM Federal Institute for Materials Research and Testing, Richard-Willstätter-Str. 11, 12489 Berlin, Germany

Dimercaptoazobenzene (DMAB) can be formed from p-Aminothiophenol (PATP) on noble metal nanoparticles by a plasmon-catalyzed reaction.[1] This reaction is oftentimes used as a model reaction for plasmonic catalysis. Many reaction parameters were shown to influence the pathway of DMAB formation. However, many aspects in the mechanism of DMAB formation are still unclear.

The mechanism of DMAB formation is studied by surface enhanced Raman scattering (SERS). It is very interesting to delineate effects due to properties of the reacting molecular species and those related to the surface properties of the plasmonic nanostructures. Currently, we achieve this e.g., by studying the roles of metal ions in the formation of DMAB on gold nanoparticles under different parameters (such as pH, laser power). Our experiments were conducted using both nanoparticle solutions and immobilized nanoparticles.[2] We perform this work, since we aim at figuring out the mechanism of plasmonic catalysis and controlling the reaction conditions precisely, exploiting the multifunctional properties of different plasmonic nanoparticles [3]. In our poster, we will show and discuss SERS data obtained in experiments at varying reaction conditions, specifically in the presence of different metal ions. Our results have implications for future sensitive detection of different reaction intermediates by plasmon-enhanced spectroscopy.



Funding by the Excellence Initiative of the German Research Foundation (DFG) in the framework of the School of Analytical Sciences Adlershof (GSC 1013 SALSA) is gratefully acknowledged. JK gratefully acknowledges funding by ERC Starting Grant No. 259432 (MULTIBIOPHOT).

References:

- [1] L. Zhao, M. Zhang, Y. Huang, C. T. Williams, D. Wu, B. Ren, and Z. Tian, *Journal of Physical Chemistry Letters*. 5 (2014), 1259–1266.
 [2] V. Joseph, M. Gensler, S. Seifert, U. Gernert, J. Rabe, and J. Kneipp. *Journal of Physical Chemistry C*, 116(2012), 6859–6865
 [3] V. Joseph, C. Engelbrekt, J. Zhang, U. Gernert, J. Ulstrup, and J. Kneipp, *Angewandte Chemie- International Edition* 51 (2012) 7592–7596.

Vesna Živanović, Christoph Arenz, Janina Kneipp¹ // Department of Chemistry and School of Analytical Sciences Adlershof (SALSA), Humboldt-Universität zu Berlin, Brook-Taylor-Str. 2, 12489 Berlin, Germany

Gold nanoparticles are used in different fields of biomedicine, including photothermal therapy, diagnostic imaging and drug delivery [1]. Liposomes constitute a leading drug delivery platform. The combination of gold nanoparticles (AuNP) and liposomes has been suggested to provide drug delivery platforms whose various physicochemical properties can be tuned to achieve better performance [2]. Release from liposomal-AuNP carriers was reported to be triggered by different stimuli, e.g., pH or light. The liposomal-AuNP delivery system allows site- and time-controlled delivery of one or multiple drugs. In order to achieve precise and effective delivery, liposomal carrier systems must be well optimized and characterized.

Surface enhanced Raman scattering (SERS) offers possibilities to characterize

drug-liposome-AuNP systems during both the preparation process and the drug delivery application. The aim of the presented work is to investigate the interaction of nanoparticles with different types of liposomes, as well as the interaction of liposomes with the drugs. Influence of liposomal composition and nanoparticles surface modification on the nanoparticles-liposome interaction will be studied. SERS data obtained from the liposomal carriers provide detailed information about their molecular composition and interaction between their components. Furthermore, the possibilities of SERS to follow changes on the single cell level [3] can be used to monitor uptake of the liposomal carriers and therapeutic effects of the drug on cells and tissues. The structure of the liposomal carriers was investigated using transmission electron and atomic force microscopies. The combined information will provide insight into the structure and composition of the liposome, and in the future may provide useful knowledge in the field of nanomedicine.

Funding by GSC 2013 SALSA and ERC grant 259432 is gratefully acknowledged.

References:

- [1] J. A. Webb and R. Bardhan. *Nanoscale* 6 (2014) 2502-2530.
- [2] T. Lajunen et al. *Journal of Controlled Release* 203 (2015) 85-98.
- [3] J. Kneipp *ACS Nano* 11 (2017) 1136-1141.

David Zopf, Jacqueline Jatschka, Sophie Thamm, André Dathe, Andrea Csáki, Wolfgang Fritzsche and Ondrej Stranik // Departement of Nanobiophotonics, Leibniz Institute of Photonic Technology e.V. (IPHT), Germany

We present a Fourier transform imaging spectrometer for the parallel read-out of sensors based on noble metallic nanoparticles supporting localized surface plasmons, which are oscillations of the particles' conduction electrons and can be excited by a free propagating light beam. The localized surface plasmon resonance (LSPR) frequency, which depends on the nanoparticles' size, shape, material and the local dielectric environment, manifests itself as a peak in the extinction and scattering spectrum of the particle. The sensor principle is based on the sensitivity of the scattering/extinction spectra upon changes of the local refractive index around the nanoparticle, such changes will be induced upon binding of molecules. The spectroscopy of metal nanoparticles shows great potential for label-free sensing. In combination with a microfluidic system our hyper-spectral imaging system allows the full spectroscopic characterization of many individual nanoparticles simultaneously. We experimentally quantified (incorporating atomic force microscopy as well) the correlation between geometry, position of plasmon resonance and sensitivity of the particles. We were able to follow the adsorption of protein layers and determined their spatial inhomogeneity with the help of hyperspectral imaging of single nanoparticles.

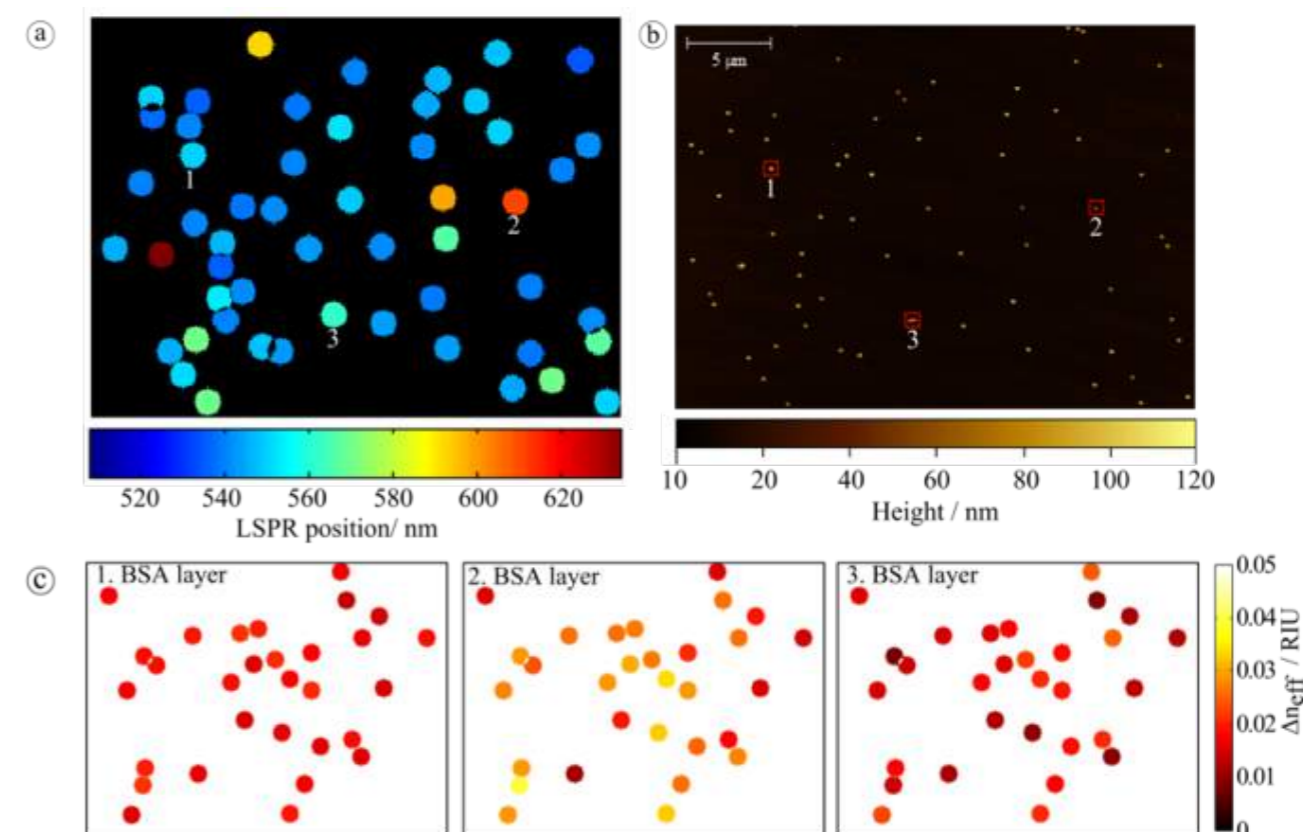


Fig. 1: (a) Lateral distribution of the elected particle ensemble, each particle is color coded according to its LSPR peak wavelength. (b) AFM-image of the region of interest shown in a). (c) False color image displaying the change of the effective refractive index on 30 single nanoparticles induced by the successive adsorption of BSA layers [1].

References:

- [1] D. Zopf, J. Jatschka, A. Dathe, N. Jahr, W. Fritzsche and O. Stranik, *Biosensors and Bioelectronics*, 2016, 81, 287.

Olga Žukovskaja^{1,2,3}, Izabella Jolan Jahn², Karina Weber^{1,2,3}, Dana Cialla-May^{1,2,3}, Jürgen Popp^{1,2,3} // ¹Friedrich Schiller University Jena, Institute of Physical Chemistry and Abbe Center of Photonics, Helmholtzweg 4, 07745 Jena, Germany / ²Leibniz Institute of Photonic Technology, Albert-Einstein-Str. 9, 07745 Jena, Germany / ³Research Campus Infectognostic, Philosophenweg 7, 07743 Jena, Germany

Pseudomonas aeruginosa is one of the most common pathogens causing respiratory tract infections, especially in the case of patients with compromised host defense mechanisms. [1] It releases several toxic metabolites, among which the most predominant one is the phenazine compound pyocyanin (PYO). PYO is specific for *P.aeruginosa*, thus it can be used as a potential biomarker. In this study, the detection of PYO was performed by surface enhanced Raman spectroscopy (SERS) combined with a microfluidic platform [2]. PYO was successfully detected in aqueous solution in the clinically relevant range (6-130 μM) with a linearity in the 0.5 μM-15 μM region and a limit of detection < 0.5 μM (Fig. 1). As next, artificial sputum was considered as matrix and prior to the measurements PYO was spiked into the matrix. In order to remove the proteins which could inhibit the successful detection of PYO, the sample was centrifuged and the obtained supernatant was measured with SERS. First results show that the components of artificial sputum dominate the recorded SERS spectra and the target analyte can be observed only for a concentration of 1 mM. However, if the SERS active nanoparticles are first mixed with the analyte and then the supernatant of the un-spiked artificial sputum is added, the sputum characteristic bands strongly decrease and PYO signatures can be observed in the SERS spectra (Fig. 2). Based on this result, a competition between PYO and the components of the artificial sputum for free binding sites on the metallic surface is concluded, with PYO representing a lower chemical affinity toward the metallic surface. Future investigations will focus on the optimization of the sample clean-up procedure in order to remove the interfering molecules from the matrix.

The funding of the grants InfectoGnostics (13GW0096F) and EXASENS (13N13856) by the Federal Ministry of Education and Research, Germany (BMBF) supporting this study is gratefully acknowledged.

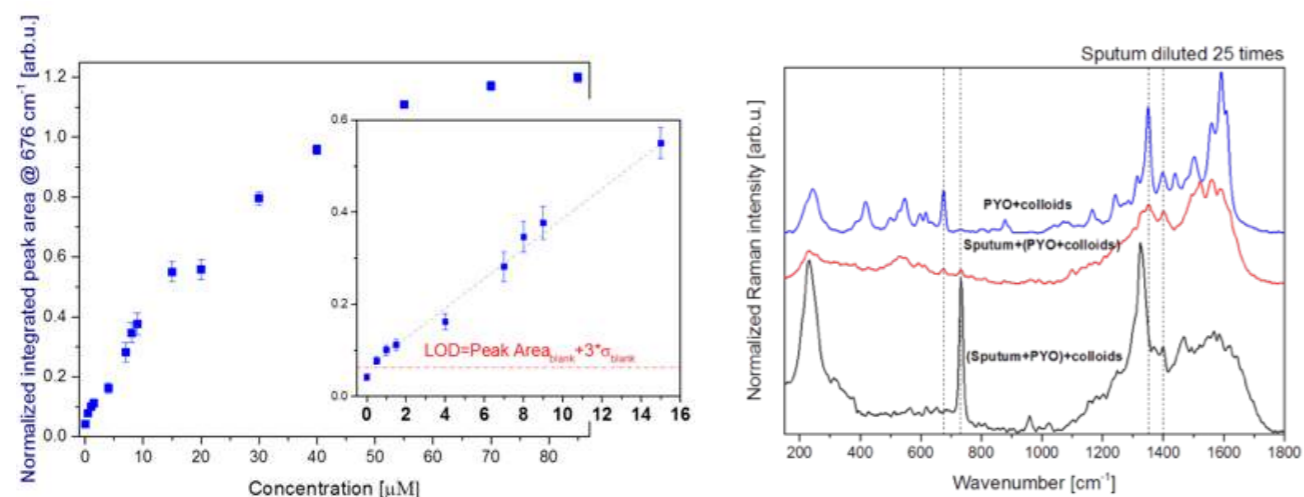


Fig. 1: Integrated peak area of the PYO Raman mode at 676 cm⁻¹ as a function of PYO concentration. In the inset linear fit and threshold lines representing the LOD values are represented, Fig. 2: SERS spectra of artificial sputum with PYO: spiked directly to sputum (black line), mixed with silver colloids and spiked to sputum (red line); SERS spectra of PYO solution for comparison (blue line)

References:

- [1] M. L. Lambert et al, Lancet Infectious Diseases 2011, 11, 30-38
- [2] T.Henkel et al, Chemical engineering journal 2004, 101, 439-445

