

MOLECULAR PLASMONICS 2023

MAY 11 – MAY 13, 2023

Leibniz IPHT // Campus Beutenberg // Jena

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PROGRAM

Organizers: Wolfgang Fritzsche & Thomas Pertsch

THURSDAY, MAY 11, 2023

Leibniz IPHT, Campus Beutenberg – Bus no. 10, 11, 12

12:00 Workshop “DNA Mitteldeutschland“ // Get-together & Lunch Buffet

13:00 Presentations

17:00 END – APPR. 30 MIN WALK TO SCHOTT VILLA

Schott Villa, Downtown – Above Westbahnhof Train Station

18:00 Get-together

18:15 Guided Museum Tour

18:45 Guided Museum Tour

19:30 DINNER

FRIDAY, MAY 12, 2023

Leibniz IPHT, Campus Beutenberg – Bus no. 10, 11, 12

8:00 Registration

9:00 Opening & Introduction // Wolfgang Fritzsche

9:05 **Plasmonic Nanoparticles**
Monitoring Cytokine Secretion by LSPR // Eiichi Tamiya (Osaka)

Optimizing Gold Nanotriangles for LSPR // Ekaterina Podlesnaia (Jena)

DNA Origami-assisted Nanoantennas // Jer-Shing Huang (Jena)

10:20 COFFEE BREAK

11:00 **Tailored Light-matter Interactions**
Light Emission Control by Metasurfaces // Thomas Pertsch (Jena)

Self-assembled Optical Antennas // Guillermo Acuna (Fribourg)

Tailored Local Fields // Bert Hecht (Würzburg)

Single-Crystal Metal Films // Gary Leach (Vancouver)

Poster Pitch Talks // Ekaterina Podlesnaia

LUNCH & POSTER SESSION

14:00 SERS & Machine Learning

Imaging and Spectroscopy at High Speed // Alexandre Brolo (Victoria)

Machine Learning-assisted SERS // Xing Yi Ling (Singapore)

Numerical Optimization of Scattering Response // Phillip Manley (Berlin)

15:15 COFFEE BREAK & POSTER SESSION

15:45 Coupling Light to Molecules

Ultra-fast Photochemistry // Jussi Toppari (Jyväskylä)

Tuning of Dielectric Metasurface // Sarah Walden (Jena)

Molecular Plasmonics and Lettuces // Bill Barnes (Exeter)

17:00 Excursion // Hike to Ernst Haeckel Monument

19:00 POSTER & BEER (& BARBECUE)

SATURDAY, MAY 13, 2023

Leibniz IPHT, Campus Beutenberg – Bus no. 10 departs downtown at 8:32 a.m.

9:00 Metal-enhanced Imaging & Sensing

Metal and Graphene Induced Energy Transfer Imaging // Jörg Enderlein (Göttingen)

Implanted Plasmonic Sensors // Carsten Sönnichsen (Mainz)

Detection of Single Proteins // Jerome Wenger (Marseille)

Plasmon-enhanced Fluorescence // Sjoerd Nootboom (Eindhoven)

10:40 COFFEE BREAK

11:00 Electron-induced Reactions & Chirality

Plasmon-induced Surface Grafting // Nordin Félidj (Paris)

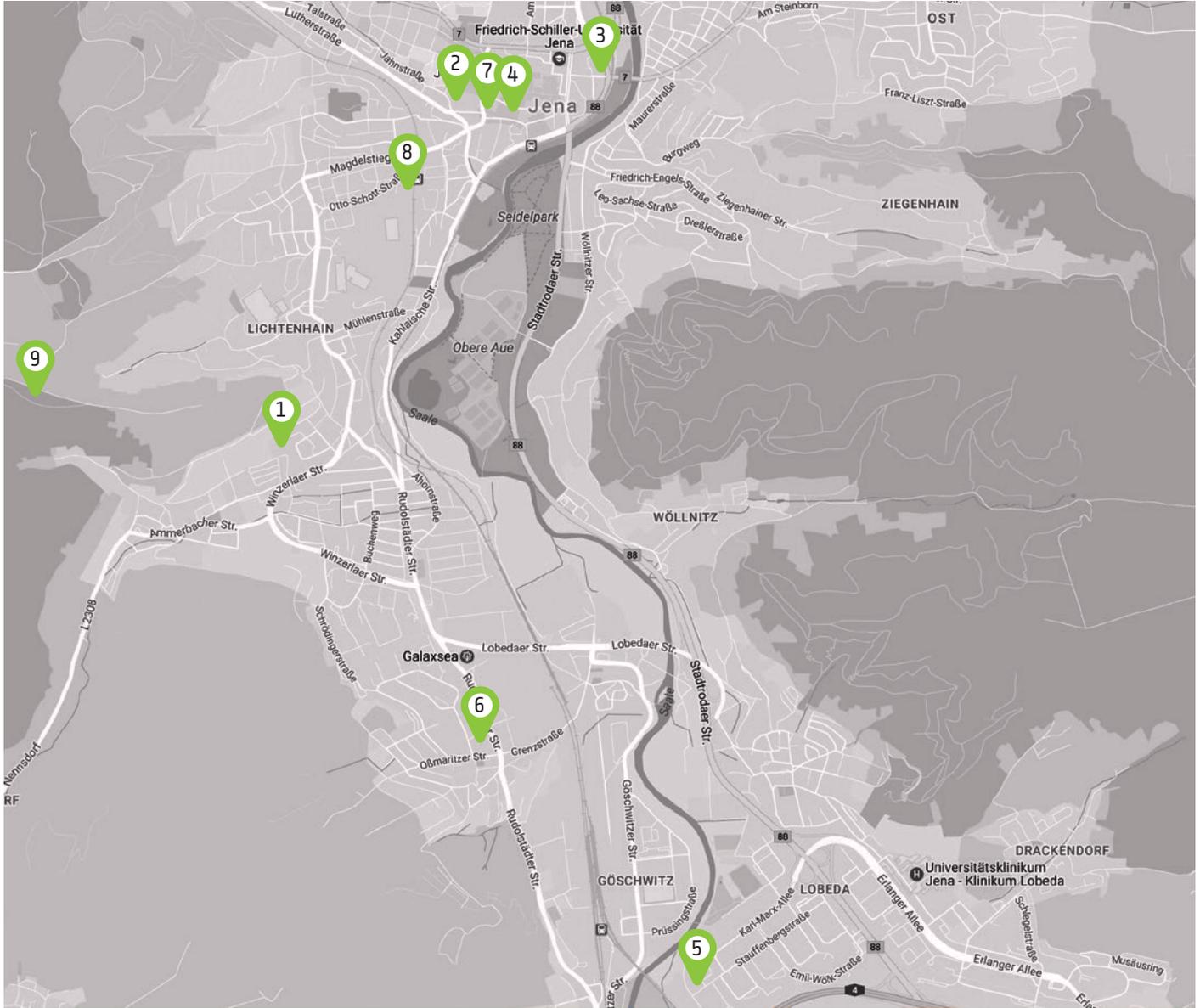
Plasmonic Activation of Nucleobases // Sergio Kogikoski Jr. (Potsdam)

Colorimetric Visualization of Chirality // Jacky Loo (Aalto)

12:15 END OF THE SESSIONS & LUNCH

LOCATION

- 1 Leibniz IPHT, Campus Beutenberg
- 2 Hotel Steigenberger Esplanade
- 3 Hotel Schwarzer Bär
- 4 Hotel Ibis
- 5 Hotel Maxx
- 6 Hotel Best Western
- 7 Bus No. 10, 11, 12
- 8 Schott Villa
- 9 Ernst Haeckel Monument



LEIBNIZ INSTITUTE OF PHOTONIC TECHNOLOGY

Nanobiophotonics Department

Albert-Einstein-Str. 9 // 07745 Jena

Phone: 0049 3641 206-304 (Office), -371 (Conference Desk) // Telefax: 0049 3641 206 344

wolfgang.fritzsche@leibniz-ipht.de

<https://www.biophotonics4future.com/plasmonics2023/>

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TALKS

Self-assembled optical antennas for controlling the emission of single molecules: unidirectionality, spectral reshaping and coupling. // Guillermo P. Acuna (Fribourg)

Molecular plasmonics and lettuces // Bill Barnes (Exeter)

Single Particle and Single Molecule SERS Imaging and Spectroscopy at High Speed //

Alexandre G. Brolo (Victoria)

Metal and Graphene Induced Energy Transfer Imaging // Jörg Enderlein (Göttingen)

Plasmon-induced surface grafting as an innovative strategy for a direct visualization of photonic modes at the origin of collective plasmonic resonances // Nordin Félidj (Paris)

Tailored local fields for strong coupling and nonlinear optics // Bert Hecht (Würzburg)

DNA origami-assisted unidirectional transmitting nanoantennas // Jer-Shing Huang (Jena)

Plasmonic activation of modified DNA nucleobases on gold and silver nanoparticles //

Sergio Kogikoski Jr. (Potsdam)

Optimum size for multi-electron reactions on plasmonic nanoparticles // Wouter Koopman (Potsdam)

Hot Electron Extraction and Spectroscopic Enhancement Enabled by Single-Crystal Metal Films and Nanostructures //

Gary W. Leach (Burnaby)

Machine Learning-Assisted Surface-Enhanced Raman Scattering // Xing Yi Ling (Singapore)

Colorimetric Visualization with Visible Chirality // Jacky Loo (Aalto)

Numerical optimization of the optical scattering response of plasmonic nanostructures // Phillip Manley (Berlin)

Direct observation of microsecond biomolecular dynamics using plasmon-enhanced fluorescence //

Sjoerd W. Nooteboom (Eindhoven)

Light emission controlled by resonant localization of light at nanostructured metasurfaces //

Thomas Pertsch (Jena)

Optimizing the synthesis of gold nanotriangles and their potential in LSPR sensing //

Ekaterina Podlesnaia (Jena)

Plasmons for sensors implanted under the skin // Carsten Sönnichsen (Mainz)

Plasmonic biosensor for cytokine detection in single immune cells // Eiichi Tamiya (Osaka)

Ultra-fast photochemistry in the strong light-matter coupling regime // Jussi Toppari (Jyväskylä)

Dual-Light responsive tuning of dielectric metasurface based on molecular photoswitches //

Sarah L. Walden (Jena)

Deep-UV autofluorescence detection of single proteins using nanophotonics //

Jerome Wenger (Marseille)

Self-assembled optical antennas for controlling the emission of single molecules: unidirectionality, spectral reshaping and coupling.

Maria Sanz, Fangjia Zhu, Aleksandra K. Adamczyk, Mauricio Pilo-Pais and [Guillermo P. Acuna](#)

Photonic Nanosystems, Department of Physics, University of Fribourg, Switzerland.

We first report on the realization of ultra-compact directional antennas for single photon emitters by means of DNA self-assembly^{1,2}. Adapting a design proposed by Pakizeh et al.³, we used the DNA origami technique to place two gold nanorods in a side-to-side (or end-fire) arrangement with an overall footprint an order of magnitude smaller than other approaches such as the optical Yagi-Uda antenna. It is worth mentioning that this design was envisioned more than a decade ago, and could only be realized recently exploiting the unique advantages of DNA nanotechnology. By coupling a single fluorescent molecule to one of the nanorods, unidirectional emission is registered red-shifted from the bonding mode when the nanorods are driven close to the antiphase mode, see Figure 1. Increasing the directionality of single emitters takes on crucial significance, for example in the context of future integrated optical circuits or quantum communication and computing schemes, which hold potential for lower energy consumption and higher efficiency using states that can be controlled up to the fundamental quantum limit.

Second, we also exploit this design to not only manipulate the directionality but also the spectrum of nearby emitters. The emission spectrum of a fluorophore is given by the energy of the possible transitions weighted by the probability of each of them to occur. By engineering the resonance of a nanoantenna, one can selectively enhance specific radiative vibronic transitions of an emitter, thus re-shaping its emission spectrum⁴ (Figure 2). In this nanometer-controlled configuration, we observe the appearance of a second fluorescence peak whose position and intensity are correlated with the resonance wavelength of the nanorod. This second peak comes from the selective enhancement of transitions to different vibrational levels of the ground state whose energy is in resonance with the nanorod's longitudinal plasmon mode. We observe that the relative intensity of these two transitions can be up to 60 times higher than in the case of an isolated molecule.

Finally, we focused on manipulating the orientation of single dyes on DNA origami in order to control the coupling with optical antennas. In particular, we exploit the ability of DNA origami to exert forces in order to "stretch" covalently incorporated dyes and deterministically align them with the orientation of double-stranded DNA helix they are located at⁵ (Figure 3). We would like to mention that our results are consistent with a work published shortly before ours⁶.



Fig. 1

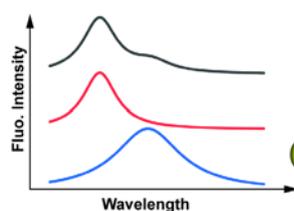


Fig. 2

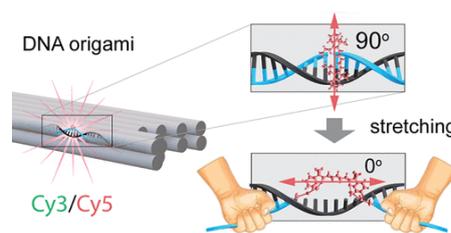


Fig. 3

Fig. 1: Sketch of an optical antenna for unidirectional emission based on two gold nanorods.

Fig. 2: A gold nanorod in the vicinity of a single dye can tune its emission spectrum

Fig. 3: Strategy to "stretch" dyes and align them with the DNA double helix of a DNA origami.

[1] Hübner et al. (2019). *Nano Lett.* 19 (9), 6629–6634.

[2] Zhu et al. (2022). *Nano Lett.* 22 (15), 6402–6408.

[3] Pakizeh et al. (2009). *Nano Lett.* 2009, 9, 2343–2349.

[4] Sanz-Paz et al. (2023). *arXiv preprint arXiv:2302.11960*

[5] Adamczyk et al. (2022). *ACS Nano*, 16 (10), 16924–16931.

[6] Cervantes-Salguero et al. (2022) *International Journal of Molecular Sciences.* 23 (14), 7690

Molecular plasmonics and lettuces

[Bill Barnes](#)

Department of Physics and Astronomy, University of Exeter, EX4 4QL< United Kingdom

Growing lettuces might not seem an obvious application area for molecular plasmonics, but the use of LEDs in urban farming is changing that perspective. LEDs are now all-pervasive in lighting applications, and these include organic LEDs. Nonetheless, there remains scope for increasing the functionality of such sources of light, for example tailoring the spectrum of the emitted light - some plants have specific optical needs!

I will provide a very brief review of the role of plasmonics in organic LEDs. I will describe on-going efforts to harness synthetic biology to optimise the interaction between molecules and plasmon modes, and I will look ahead to see how strong coupling of molecules and plasmons may help deliver greater functionality.

Single Particle and Single Molecule SERS Imaging and Spectroscopy at High Speed

[Alexandre G. Brolo](#)

Department of Chemistry, University of Victoria, Victoria, BC, Canada, V8W 2Y2
(agbrolo@uvic.ca)

Surface-enhanced Raman scattering (SERS) is a promising technique for applications in analytical chemistry due to its high sensitivity and selectivity [1]. However, the fully implementation of SERS as analytical tool can be challenging due to fluctuations in SERS intensities observed from diluted solutions, which complicate quantification. Those types of fluctuations have been assigned to evidence of single-molecule detection by SERS [2]. Recently, we have developed new experimental methods capable of monitoring those fluctuations at high speed (sub-ms time scale). It is clear that, at those high-speed time scale, the SERS fluctuations are a more general phenomenon that can be observed even from single nanoparticles [3].

Figure 1a shows an example of Raman imaging from a single nanoparticle fully-coated with an organic thiol probe. The SERS image of individual nanoparticles, as in Figure 1a, were acquired at ~600 fps. Figure 1b shows the time trace for the SERS intensity in one of the nanoparticles. The fluctuations in SERS intensity observed in Figure 1b are very evident and they were observed for different combinations of nanoparticles – molecule systems. Super-resolution spectroscopy methods (STORM) was applied to determine the spatial origin of those fluctuations [4]. The results suggest that different hotspots in the same nanoparticle are activated at different time scale. This new high-speed method reveals some important fundamental characteristics of SERS hotspots that can be useful for analytical applications.

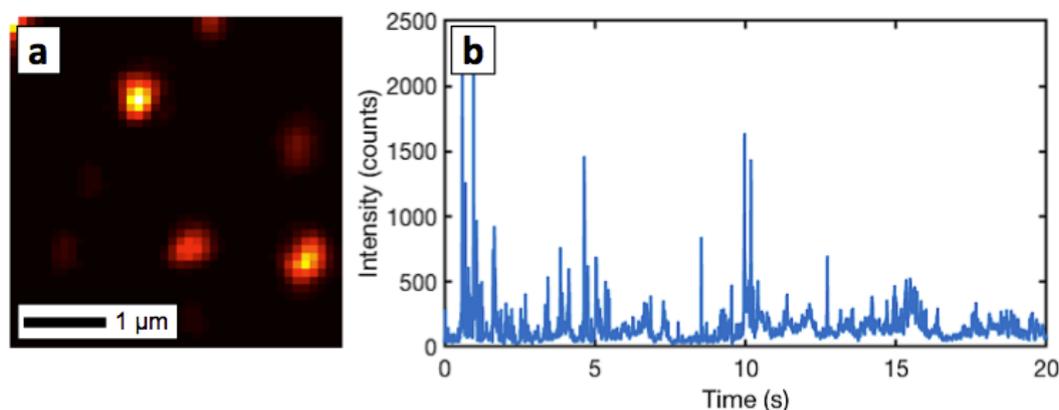


Figure 1: (a) SERS images of individual nanoshells. (b) Time-dependent SERS intensity fluctuations.

[1] Fan M., de Andrade G FS. and Brolo AG, *Anal. Chim. Acta* (2020); 1097, 1.

[2] Le Ru EC, Etchegoin PG, *Ann. Rev. Phys. Chem.* (2012); 63, 65.

[3] Lindquist NC., de Albuquerque CD, Sobral-Filho RG, Paci I, and Brolo AG, *Nature Nanotech* (2019); 14, 981.

[4] de Albuquerque CD, Hokanson K, Thorud S, Sobral-Filho RG, Lindquist NC., Brolo AG, *ACS Photonics*; (2020) 7, 434.

Metal and Graphene Induced Energy Transfer Imaging

Jörg Enderlein

Third Institute of Physics – Biophysics, Georg August University, Göttingen, Germany, jenderl@gwdg.de

Metal-Induced Energy Transfer (MIET) Imaging is a recently developed method [1] that allows for nanometer resolution along the optical axis. It is based on the fact that, when placing a fluorescent molecule close to a metal, its fluorescence properties change dramatically, due to electromagnetic coupling of its excited state to surface plasmons in the metal. This is very similar to Förster Resonance Energy Transfer (FRET) where the fluorescence properties of a donor are changed by the proximity of an acceptor that can resonantly absorb energy emitted by the donor. In particular, one observes a strongly modified lifetime of its excited state. This coupling between an excited emitter and a metal film is strongly dependent on the emitter's distance from the metal. We have used this effect for mapping the basal membrane of live cells with an axial accuracy of ~3 nm. The method is easy to implement and does not require any change to a conventional fluorescence lifetime microscope; it can be applied to any biological system of interest, and is compatible with most other super-resolution microscopy techniques that enhance the lateral resolution of imaging [2-4]. Moreover, it is even applicable to localizing individual molecules [5-6], thus offering the prospect of three-dimensional single-molecule localization microscopy with nanometer isotropic resolution for structural biology [7]. I will also present latest developments of MIET where we use a single layer of graphene instead of a metal film that allows for increasing the spatial resolution down to a few Ångströms [8-10].

- [1] Chizhik, A. I., Rother, J., Gregor, I., Janshoff, A., & Enderlein, J. (2014). *Nature Photonics* **8**:124-127.
- [2] Baronsky, T., Ruhlandt, D., Brückner, B. R., Schäfer, J., Karedla, N., ... & Chizhik, A. I. (2017). *Nano Lett.* **17**:3320-3326.
- [3] Chizhik, A. M., Ruhlandt, D., Pfaff, J., Karedla, N., Chizhik, A. I., ... & Enderlein, J. (2017). *ACS Nano* **11**:11839-11846.
- [4] Chizhik, A. M., Wollnik, C., Ruhlandt, D., Karedla, N., Chizhik, A. I., ... & Rehfeldt, F. (2018). *Mol. Biol. Cell* **29**:846-851.
- [5] Karedla, N., Chizhik, A. I., Gregor, I., Chizhik, A. M., Schulz, O., & Enderlein, J. (2014). *ChemPhysChem* **15**:705-711.
- [6] Isbaner, S., Karedla, N., Kaminska, I., Ruhlandt, D., Raab, M., Bohlen, J., ... & Tsukanov, R. (2018). *Nano Lett.* **18**:2616-2622.
- [7] Thiele, J.C., Jungblut, M., Helmerich, D., Tsukanov, R., Chizhik, A., Chizhik, A.I., Schnermann, M., Sauer, M., Nevskiy, O., Enderlein, J. (2022). *Science Adv.* **8**:14190-14200.
- [8] Ghosh, A., Sharma, A., Chizhik, A. I., Isbaner, S., Ruhlandt, D., Tsukanov, R., Gregor, I., Karedla, N., & Enderlein, J. (2019). *Nature Photonics* **13**:860-865.
- [9] Raja, S. O., Chizhik, A. I., Schmidt, C. F., Enderlein, J., & Ghosh, A. (2021). *Nano Letters* **21**:8244-8249.
- [10] Ghosh, A., Chizhik, A. I., Karedla, N., & Enderlein, J. (2021). *Nature Protocols* **16**:3695-3715.

Plasmon-induced surface grafting as an innovative strategy for a direct visualization of photonic modes at the origin of collective plasmonic resonances

T. Geronimi-Jourdain¹, M. Braïk², A. Belkhir², S. Lau-Truong¹, A. Chevillot-Biraud¹, C. Mangeney³, N. Félidj¹

¹ Université Paris Cité, CNRS, ITODYS, F-75006 Paris, France

² Laboratoire de Physique et Chimie Quantique, Université Mouloud Mammeri, Tizi-Ouzou, Algérie

³ Université Paris Cité, CNRS, LCBPT, F-75006 Paris, France

Plasmonic nanostructures arranged in regular arrays support lattice plasmon modes, resulting from the diffraction of photonic modes of different orders in the plan of the substrate (here indium tin oxide, ITO). These lattice modes are characterized by a reduced linewidth of the resonance, and an important improvement in its quality factor [1]. Therefore, such arrays can provide improved platforms in the context of non-linear optics, molecular sensing, plasmon-based lasers, or surface enhanced spectroscopies. In this work, we show that we are able to visualize directly in the real space, the photonic modes propagating on the ITO substrate, at the origin of surface lattices (see figure below).

For this visualization, we use a strategy based on a plasmon-induced grafting of diazonium salts [2]. The observation of these photonic modes is of crucial importance in order to identify the nature of these lattice modes.

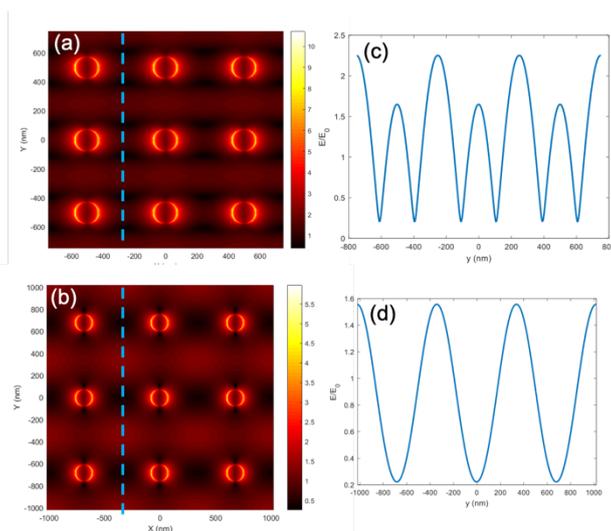


Fig. : Figures (a) and (b): mapping of the intensity of the electric field, obtained by the FDTD method, of two regular arrays of gold disks (diameter 150 nm, height 50 nm, on an ITO layer), for a grating constant of (a) 500 nm, and (b) 680 nm. The graphs (c) and (d) display the profile of the intensity corresponding to the vertical dashed lines in (a) and (b), respectively. The profile in (c) evidences the photonic mode of the (1,0) order related to the mapping in (a), and the profile in (d), the photonic mode of the (1,1) order related to the mapping in (b).

[1] I. Ragheb et al., *J. Opt. Soc. Am. B* **36**, E36-E41 (2019).

[2] I. Kherbouche et al., *Nanoscale*, **13**, 11051-11057 (2021)

Tailored local fields for strong coupling and nonlinear optics

[Bert Hecht](#), [Jessica Meier](#), [Luka Zurak](#), [Rene Kullock](#), [Andrea Locatelli](#), [Daniel Friedrich](#), [Jin Qin](#), [Benedikt Schurr](#), [Thorsten Feichtner](#)

Nano-Optics & Biophotonics group, Experimental Physics 5, Physics Institute, University of Würzburg, Am Hubland, D-97074 Würzburg, Germany

He-ion beam milling of monocrystalline gold and silver flakes offers new possibilities to tailor local fields since it allows to fabricate structural details with an unprecedented precision of 1 nm. We exploit these capabilities to fabricate resonant optical antennas exhibiting a global antisymmetric mode which causes very high field enhancement in the gap. We then locally break the symmetry of the antenna hotspot to efficiently generate second harmonic radiation by switching of the silencing effect (see Fig. 1).

In another application we tailor plasmonic nanoslit resonators with very small modal volumes to fit the transition energy of single quantum dots. We exploit a photoactivated oxygen driven blueshift of the quantum dot emission to tune its photoluminescence spectrum over that of the nanoslit resonance. As a result, we observe complete anticrossing spectra at ambient conditions (see Fig. 2).

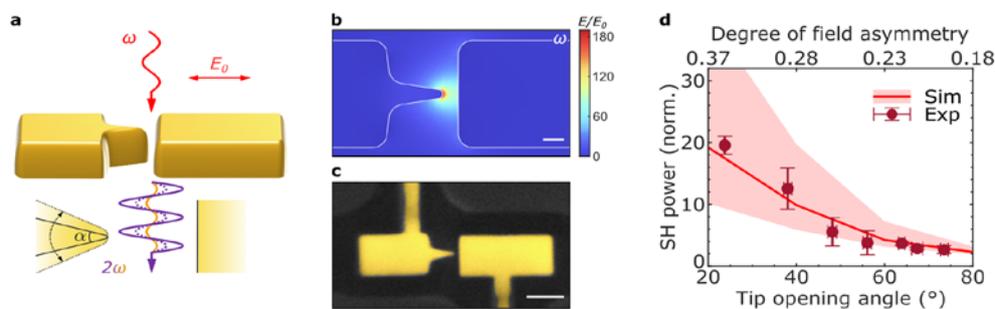


Fig. 1: Effect of local symmetry breaking on the SHG process in gold nanoantennas. a, Scheme of the SHG process from an asymmetric-gap antenna. b, Linear field enhancement plot. Scale bar, 10 nm. c, Scanning electron micrograph of an asymmetric-gap antenna with tip apex radius of 3 nm and gap size of 8 nm. Scale bar, 50 nm. d, Tuning SHG emission by variation of the local degree of asymmetry.

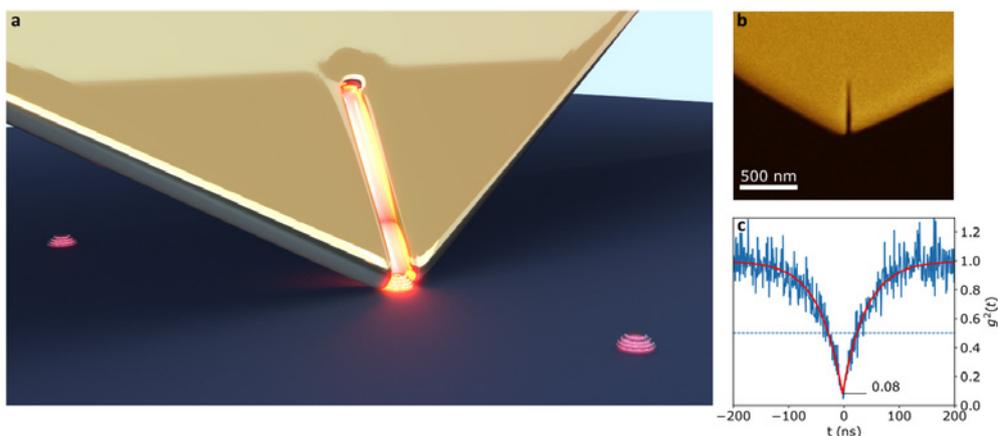


Fig. 2: A gold microplatelet scanning plasmonic nanoresonator in close contact to a quantum dot (artistic representation). b SEM image of a fabricated PNR. c 2nd-order autocorrelation function, g_2 , of an individual QD.

[1] Second harmonic generation from plasmonic hotspots by controlled local symmetry breaking, J. Meier, L. Zurak, A. Locatelli, T. Feichtner, R. Kullock, B. Hecht, submitted (2023), arXiv:2210.14105.

DNA origami-assisted unidirectional transmitting nanoantennas

Ayşe Tuğça Mina Yeşilyurt,^{a‡} Maria Sanz-Paz,^{b‡} Fangjia Zhu,^b Karthika S. Sunil,^a Xiaofei Wu,^a Guillermo P. Acuna,^{b*} Jer-Shing Huang^{a,c,d,e*}

a. Leibniz Institute of Photonic Technology, Albert-Einstein-Straße 9, 07745 Jena, Germany

b. Department of Physics, University of Fribourg, Chemin du Musée 3, Fribourg CH-1700, Switzerland.

c. Institute of Physical Chemistry and Abbe Center of Photonics, Friedrich-Schiller-Universität Jena, D-07743 Jena, Germany.

d. Research Center for Applied Sciences, Academia Sinica, Taipei 11529, Taiwan.

e. Department of Electrophysics, National Yang Ming Chiao Tung University, Hsinchu 30010, Taiwan

Confining the emission of single quantum emitters into a pre-defined direction is of great interest for the applications of single-photon sources. Plasmonic nanoantennas enable the control and manipulation of radiation from single quantum emitters. Previous efforts mostly rely on the interference of coherent waves from multiple resonators [1,2]. The performance depends on the number of resonating elements, making the top-down fabricated unidirectional nanoantennas bulky [1]. Recently, DNA origami technology has been used to produce unidirectional nanoantennas with one emitter and two nanorods [2]. However, further enhancing the directionality by increasing the number of resonant elements would be technically demanding. Here, we demonstrate ultracompact DNA origami-assisted unidirectional nanoantennas (footprint ~ 150 nm) based on Kerker condition, the balanced interference of the induced electric (ED) and magnetic dipole (MD) in the same structure (Fig. 1a). The meta-emitter consists of three gold nanoparticles and a single dye molecule (Atto647N) on a precisely engineered DNA origami template. To bring the emitter to the center of the gap, the DNA origami was designed to capture one of the three gold nanospheres (diameter = ~ 70 nm) on the opposite side of the triangular origami template (Fig. 1b). Trimer nanoantennas were obtained at high yield (Fig. 1c) and the emission of the single dye molecule show clear unidirectionality. The largest front-to-back emission ratio (F/B) was found to be more than 10 dB (Fig. 1d).

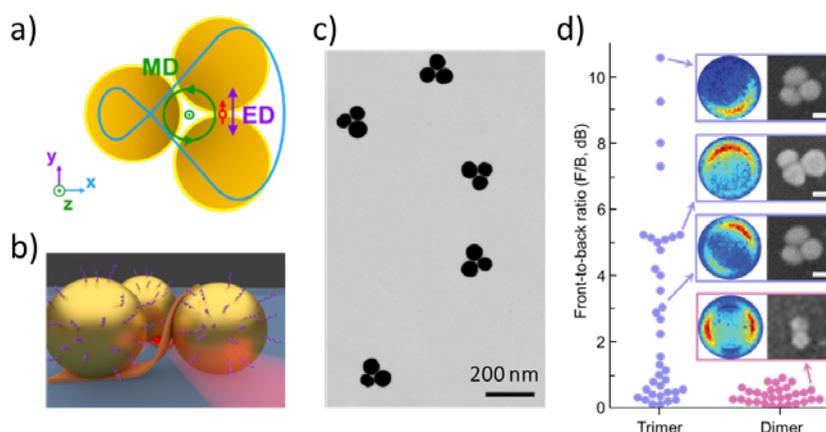


Fig. 1: a) Configuration of the trimer nanoantenna driven by a single emitter (red arrow). The unidirectional radiation pattern (blue contour) stems from the balanced interference of the electric dipole (ED) and magnetic dipole (MD). b) A schematic showing how the curved origami template brings the single emitter to the dimer gap. c) An SEM image of the DNA origami-assisted trimer nanoantennas. d) Representative emission patterns and SEM images of trimer and dimer antennas. Distinct directionality (F/B ratio in dB) is found between trimers (purple dots) and dimers (pink dots).

[1] See K-M, Lin F-C, Chen T-Y, Huang Y-X, Huang C-H, Yeşilyurt A T M, Huang J-S. Photoluminescence-Driven Broadband Transmitting Directional Optical Nanoantennas *Nano Lett.* 2018; 18: 6002-6008.

[2] Zhu F, Sanz-Paz M, Fernández-Domínguez A I, Zhuo X, Liz-Marzán L M, Stefani F D, Pilo-Pais M, Acuna G P. DNA-Templated Ultracompact Optical Antennas for Unidirectional Single-Molecule Emission. *Nano Lett.* 2022; 22: 6402-6408.

Plasmonic activation of modified DNA nucleobases on gold and silver nanoparticles

Sergio Kogikoski Jr.^a, Marcel Grünheid^a, Christina Beresowski^a, João .F.F. Ameixa^a, Janusz Rak^b, Ilko Bald^a

^aInstitute of Chemistry, University of Potsdam, 14476, Potsdam, Germany.

^bFaculty of Chemistry, University of Gdansk, 80308, Gdansk, Poland.

Modified nucleobases, either pyrimidines or purines, are very good candidates of molecules to react with low energy electrons.¹ On the other hand, plasmonic nanoparticles upon light irradiation generate a pair of hot-electron and hot-hole with low energy that can react with such modified nucleobases. Our group have already shown that the purines bromoadenine and bromoguanine are reactive towards hot-electrons generated by Au and Ag nanoparticles, both isolated and also when included in DNA oligomers, and that the main control of the reaction is the interface electrochemical potential between the nucleobase and the metal nanoparticle.^{2,3} Herein we used uracil derivatives, namely halogenated thiouracil and halogenated uracil, to test if such molecules are reactive towards the plasmonically generated hot-charges, Figure 1A. Surface-enhanced Raman spectroscopy is a very powerful tool to study plasmonic reactions, since the reactions are activated by the light, and the same light is used to probe the molecules modifications by variations in the vibrational spectra, Figure 1B. The obtained results showed that the bromo- and iodo-thiouracil can be activated using hot-carriers generated by the plasmonic nanoparticles, on the other hand bromo- and iodo-uracil are not affected by the light-induced reaction. Our results are fundamental to further understand the molecular bases on how certain molecules are activated by plasmons to further comprehend the specific molecular features that enable certain molecules to be used in plasmonic catalysis.

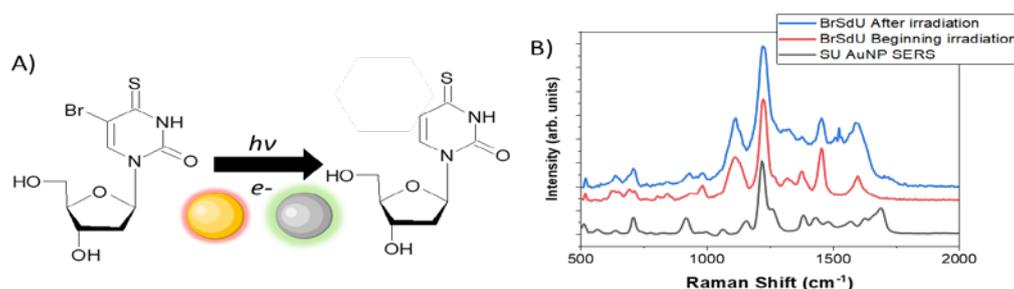


Figure 1. A) Scheme showing the reaction of bromothiouracil adsorbed on plasmonic nanoparticle, and the generation of thiouracil. B) SERS spectra bromothiouracil (BrSdU) before and after irradiation and the spectra of thiouracil (SU) for comparison.

[1] R. Schürmann, S. Vogel, K. Ebel and I. Bald, *Chemistry - A European Journal*, 2018, **24**, 10271–10279.

[2] S. Kogikoski, A. Dutta and I. Bald, *ACS Nano*, 2021, **15**, 20562–20573.

[3] A. Dutta, R. Schurmann, S. Kogikoski, N. S. Mueller, S. Reich and I. Bald, *ACS Catal*, 2021, **11**, 8370–8381.

Optimum size for multi-electron reactions on plasmonic nanoparticles

Wouter Koopman, Mareike Wübbenhorst, Kyra Peikert, Felix Stete, Matias Bargheer

Institut für Physik und Astronomie, Universität Potsdam, Karl-Liebknecht-Str. 24/25, 14476
Potsdam, Germany

Noble-metal nanoparticles with visible broad-band absorption provide promising photocatalysts for photo-driven redox reactions, including demanding multi-electron reaction such as the reduction of CO_2 [1], or the much-researched $\text{N} = \text{N}$ coupling [2]. An important advantage of such nanoparticles is the tunability of their optical properties by modification of the particle geometry. At the same time, modifications of the particle size and shape also influence its chemical activity, at least through changes of the surface-to-volume ratio. This leads to complex interplay of chemical and optical influences on the photo-redox activity of a particular nanoparticle.

In this talk, I will discuss the differences in particle size-dependence for a photo-redox processes involving either a one- or a two-electron oxidation half-reaction. While for single electron-transfer processes smaller particles are generally preferred, the situation is fundamentally different for photo-redox processes involving at least one multi-electron half-reaction. Our research shows a clear size-optimum for the quantum efficiency in this case. We relate this observation to the limited lifetime of the reaction intermediate and were able to describe it by the Poissonian absorption of photons on a single particle level. These results give a fundamental insight in the mechanism underlying the photo-reactivity of plasmonic metal nanoparticles.

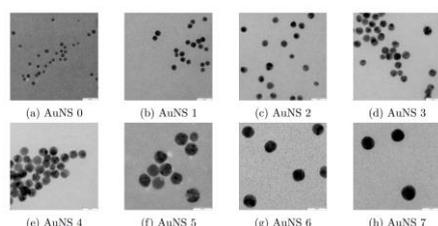


Fig. 1

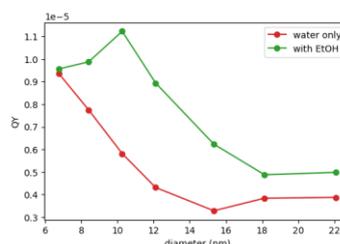


Fig. 2

Fig. 1: Layered-growth mechanism for gold nanoparticles allows a very precise control over its size.
Fig. 2: The reaction quantum yield shows a clear size optimum if the two-electron oxidation of ethanol is involved.

[1] Devasia, (2021) *Nat Commun*, 12 (1), 2612.

[2] Koopman, *Adv. Mater. Interf.* (2021), 8 (22), 2101344

Hot Electron Extraction and Spectroscopic Enhancement Enabled by Single-Crystal Metal Films and Nanostructures

Finlay C. MacNab, Sasan V. Grayli, [Gary W. Leach](#)

Simon Fraser University, 8888 University Dr. Burnaby, BC Canada V5A 1S6 gleadh@sfu.ca

Surface plasmons concentrate the extended three-dimensional fields of propagating electromagnetic waves to nanometer-scale structures, where their enhanced and confined local fields can drive new physical and chemical phenomena. Plasmon-mediated hot carrier generation is particularly interesting and can provide a means for direct energy harvesting, photocatalytic chemistry, and the development of new optical sensor technologies. However, identifying and optimizing the factors that lead to efficient hot electron extraction have remained a challenge and have limited the utility of surface plasmon-based devices for these applications. Here, we describe the requirements for efficient hot electron extraction in smooth and nanostructured Ag/ZnO plasmonic photovoltaic devices (Fig. 1). Device efficiency is found to be highly correlated with material quality and the electronic character of the interfaces.

Our findings have driven the development of a new scalable and environmentally friendly electroless deposition method for single-crystal epitaxial noble metals films and nanostructures.[1] The method produces smooth, low-loss, single-crystal noble metal films ideal for subtractive patterning of nanostructures through ion beam milling, and high definition, sub-wavelength single-crystal nanostructured arrays through lithographic patterning. We describe the nucleation and growth of these metal films and nanostructures in the absence and presence of anionic shape-control agents and examine the role of specific anions in determining the resulting film and nanostructure morphologies via scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HRTEM).[2] These effects have been exploited to yield large area patterned, and shape-controlled nanoarrays of single-crystal metal nanostructures, yielding plasmonic metasurfaces with tailored local fields that can be tuned to exploit local field enhancements (Fig. 2). These approaches offer new and cost-effective routes to achieve crystalline, shape-controlled surface nanostructure for nanophotonic and nanodevice applications.

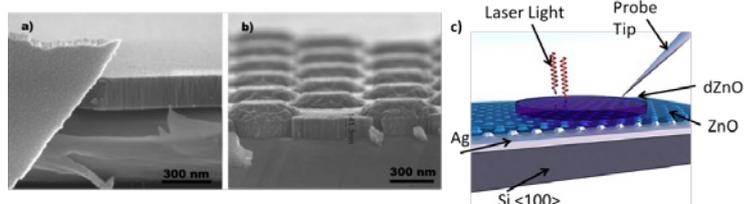


Fig. 1

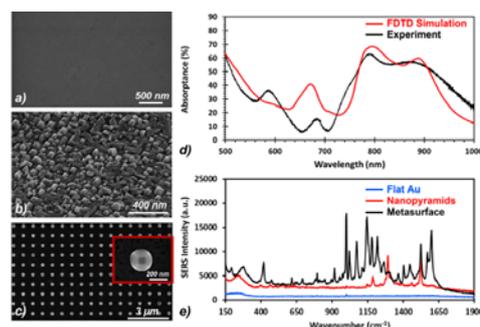


Fig. 2

Fig. 1: ZnO deposited on single-crystal a) planar and b) nanostructured Ag(100) to form plasmonic photovoltaic (PV) structures. c) device structure for free space-coupled PV measurements.
Fig. 2: SEM images of a) flat Au, b) randomly distributed square nanopillars, c) a 250 nm diameter, 700 nm period, shape-controlled gold metasurface. d) Experimental and FDTD simulated absorbance of the benzoic acid-coated metasurface shown in c). 785 nm-induced SERS response from the benzoic acid-coated surfaces displayed in panels a-c).

[1] V. Grayli, S.; Zhang, X.; MacNab, F.C.; Kamal, S.; Star, D.; Leach, G. W., Scalable, Green Fabrication of Single-Crystal Noble Metal Films and Nanostructures for Low-Loss Nanotechnology Applications., ACS Nano, (2020) 14, 7581–7592.

[2] V. Grayli, S.; Zhang, X.; Star, D.; Leach, G. W., "Shape-Controlled, Single-Crystal Gold Surface Nanostructures", (2019) ChemRxiv.9956450.v1, published online Oct. 11, 2019.

Machine Learning-Assisted Surface-Enhanced Raman Scattering

[Xing Yi Ling](#)

School of Chemistry, Chemical Engineering and Biotechnology, Nanyang Technological University, Singapore

Surface-enhanced Raman scattering (SERS) is a molecule-specific spectroscopic technique with diverse applications in (bio)chemistry, clinical diagnosis and toxin sensing. It leverages on intense electromagnetic (EM) fields from localized surface plasmon resonance (LSPR) in plasmonic nanoparticles to enhance molecular detection. In this talk, I will discuss my group's effort in using molecular enhancement strategies and machine learning algorithms to bolster SERS performance for biomedical applications. First, I will discuss various chemical and physical modification strategies of nanoparticles to bestow desirable chemoselectivity and increase target analyte/biomarker affinity to achieve higher detection sensitivity and selectivity. I will also evaluate how chemometrics and machine learning algorithms can transform the assimilation and interpretation of complex spectral data in biological samples by discerning more patterns hidden within the data, to achieve high throughput data analysis, sensitivity, and disease prediction. I hope these insights can stimulate the development of innovative and hybrid detection methods across the entire analytical discipline to resolve longstanding challenges in biological biomarker and analyte sensing and detection.

Colorimetric Visualization with Visible Chirality

Jacky Loo¹, Minh-Kha Nguyen¹, Yike Huang¹, Susanna Hällsten¹, Kalle Oskari Mikkola¹, Tim Liedl², Anton Kuzyk¹

¹ Department of Neuroscience and Biomedical Engineering, School of Science, Aalto University, FI-00076 Aalto, Finland

² Faculty of Physics and Center for NanoScience (CeNS), Ludwig-Maximilians-University, Geschwister-Scholl-Platz 1, 80539 Munich, Germany

Chiral structures with pronounced optical activities have the potential to facilitate colorimetric readout and allow for easy naked-eye detection of chiroptical responses. DNA origami has been widely used with plasmonic nanoparticles to generate reconfigurable chiral plasmonic metamolecules (CPM) that exhibit dynamic chiral optical responses. However, reported optical activities, typically below 2% in terms of dissymmetry factor (g -factor), can only be detected using CD spectrometry, rather than colorimetric techniques. Although chiral nanoparticles could be fabricated to obtain a superior optical activity (g -factor of up to 20%), it is currently limited to static structures.

In this work, I will present fabrication of CPM with a g -factor that is high, switchable (from 1 to 16%), and tunable across the visible spectrum. Colorimetric visualization of CPMs with a high g -factor at sub-nM concentrations was achieved. Moreover, the responsive plasmonic nanoswitches, which shows dynamic g -factor change in relation to the special configuration of our CPM, was engineered for molecular biosensing for various types and sizes of biomolecules. Addition of target analytes resulted in a drastic color change that could be readily detected with the naked eye. The detection limit of a protein analyte was down to femtomole without any further signal amplification.

We anticipate that our approach will advance plasmonic sensing schemes and create new opportunities for developing other applications based on reconfigurable plasmonics.

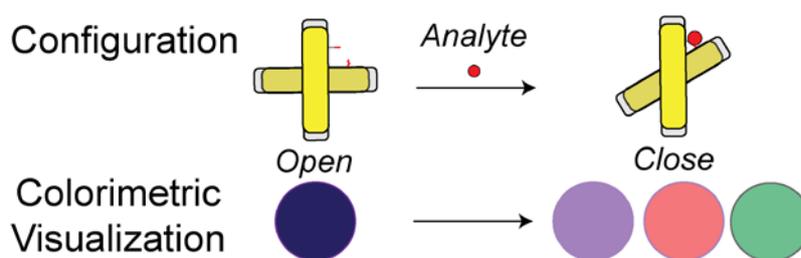


Figure 1. Schematics of the fabricated CPM responsive to target analyte and the colorimetric visualization scheme. The addition of target analyte changes the special configuration of our CPM (from open→close configuration) resulting in a visual color change.

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Numerical optimization of the optical scattering response of plasmonic nanostructures

Fridtjof Betz¹, Felix Binkowski¹, [Phillip Manley](#)^{1,2}, Martin Hammerschmidt^{1,2}, Lilli Kuen^{1,2}, Matthias Plock¹, Phillip-Immanuel Schneider^{1,2}, Ivan Sekulic^{1,2}, Lin Zschiedrich^{1,2}, Sven Burger^{1,2}

1) Zuse Institute Berlin, 14195 Berlin, Germany

2) JCMwave GmbH, Bolivarallee 22, 14050 Berlin, Germany

Modern fabrication methods allow for the fabrication of plasmonic nanostructures at high accuracies. This allows for highly efficient plasmonic devices in which electromagnetic field energy may be concentrated to very small volumes. Results from theoretical physics provide models that accurately describe physical processes in complex setups. However, in order to reach efficient designs which optimize specific interactions, numerical simulations and optimizations are frequently used, as these can be applied to arbitrary geometrical settings, are significantly easier to realize than experimental optimization setups, and may provide additional insight.

In this contribution we will discuss numerical simulation methods and machine learning based optimization algorithms (1,2) which have recently been developed in our group. In particular, we will discuss hp finite element methods and Bayesian optimization based on Gaussian processes. Furthermore, we will discuss recent applications of these methods to various nanoplasmonic and nanophotonic settings. These include nanoplasmonic, chiral and achiral setups for sensing, photo-chemistry, and photovoltaics (3-8). We will in particular focus on chiral interactions in plasmonic setups assembled by DNA-origami.

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[2] F. Binkowski, et al., *Commun. Phys.* 5, 202 (2022)

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[4] K. Martens, et al., *Nat. Commun.* 12, 2025 (2021)

[5] S. Rej, et al., *Nano Energy* 104, 107989 (2022)

[6] M. Dass, et al., *Mater. Adv.* 3, 3438 (2022)

[7] F. Binkowski, et al., *ACS Photon.* 8, 1243 (2021)

[8] P. Tillmann, et al., *Opt. Express* 29, 22517 (2021)

Direct observation of microsecond biomolecular dynamics using plasmon-enhanced fluorescence

Sjoerd W. Nooteboom¹, Kasper Okholm², Duncan Sutherland², Peter Zijlstra¹

¹Eindhoven University of Technology, De Rondom 70, 5612AP Eindhoven, The Netherlands

²Aarhus University, Nordre Ringgade 1, 8000 Aarhus C, Denmark

Biomolecules such as DNA are at the basis of all processes in living organisms. These molecules exhibit intra- and intermolecular interactions on timescales from nanoseconds to hours. Understanding such mechanisms is key to solving problems in many fields including medicine. Typically, these mechanisms are studied using single-molecule Förster resonance energy transfer (smFRET).¹ This is a powerful technique that allows for the observation of real-time biomolecular dynamics while revealing spatial and temporal heterogeneity. However, the brightness and photon budget of the required fluorophores are limited by saturation and bleaching, prohibiting direct observation of sub-ms processes in most cases.² Methods based on optical tweezers have better time resolution, but are not force-free.³

In this work, we use the strong plasmonic fluorescence enhancement provided by gold nanorods (AuNRs)⁴ to harvest on the order of 10 million photons/s from a single fluorophore, dramatically increasing the signal-to-noise ratio at short timescales. Using methods based on DNA-PAINT,⁵ we study the behavior of several DNA constructs such as hairpins and Holliday junctions (Fig. 1) on the single-molecule level.

We also exploit the strong field gradients around the AuNR, which lead to spatial variations in fluorescence enhancement factor. This allows us to directly observe real-time kinetics and dynamics of the DNA constructs on timescales down to 10 μ s (Fig. 2).

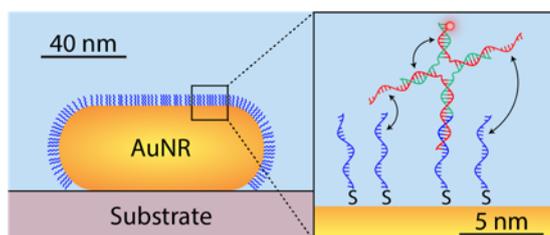


Fig. 1

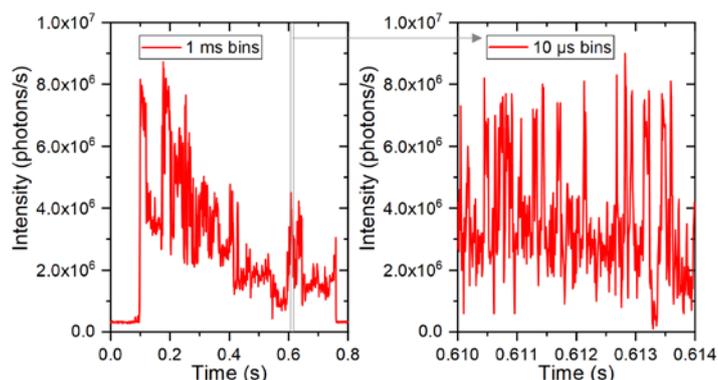


Fig. 2

Fig. 1: Schematic illustration of DNA-PAINT performed with a Holliday junction on AuNRs.

Fig. 2: Left, dynamics of the Holliday junction measured with 1 ms binning. Right, zoom-in of the left figure with 10 μ s binning.

[1] Bandyopadhyay, D.; Mishra, P. P. (2021). *Front. Mol. Biosci.*, 8 (September), 1–18.

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[5] Nooteboom, S. W.; Wang, Y.; Dey, S.; Zijlstra, P. (2022). *Small*, 18 (31), 2201602.

Light emission controlled by resonant localization of light at nanostructured metasurfaces

Thomas Pertsch^{1,2,3}

- 1) Friedrich Schiller University Jena, Abbe Center of Photonics, Institute of Applied Physics, Albert-Einstein-Straße 15, 07745 Jena, Germany
- 2) Fraunhofer Institute for Applied Optics and Precision Engineering, Albert-Einstein-Straße 7, Jena 07745, Germany
- 3) Max Planck School of Photonics, Hans-Knöll-Straße 1, 07745 Jena, Germany

The resonant localization of electromagnetic fields at nanostructures allows to control the fundamental emission processes of light, where primarily, we exploit three such mechanisms. First, the resonance frequency of the electromagnetic modes can be tuned to the transition frequency of the light emitters. Second, the field profile of the electromagnetic modes can be matched to the emitters' transition state. And third, the nonlinearity of the nanostructured material can be exploited for frequency conversion to render the emission frequency different from the excitation light.

In this presentation, we will give an overview of our recent activities towards the control of light emission by resonant localization of light at nanostructured metasurfaces. Here, metasurface are formed by an ensemble of nanoresonators placed in a regular fashion on a dielectric substrate. The individual resonant nanostructures, which are often also called the metaatoms, are made of dielectrics, metals, and semiconductors. Besides their intrinsic nonlinearity, the functionality of the metaatoms for the control of light emission, can be enhanced by coupling to semiconductor quantum dots or atomically thin membranes of semiconductors.

On the one hand, the electromagnetic modes of metasurfaces can be controlled by the material and geometry of the individual metaatoms. On the other hand, also the placement of the metaatoms in the overall ensemble forming the metasurface has a strong influence on the mode spectrum. There are a number of different resonance mechanisms underlying the formation of these modes, ranging from so-called Mie modes, which are localized mainly in the individual metaatoms, to Fano-type resonances or so-called Bound States in the Continuum (BIC), which usually occupy several metaatoms.

Overall, the combination of metasurfaces with light-emitting materials offers a rich field to control the emission of light in many parameters, ranging from its efficiency, spectral distribution, polarization, and angular distribution to the quantum-properties of light, as e.g. photon-pair correlations or entanglement. Our report will cover examples of most of these aspects.

[1] F. Vitale, et al., *Applied Physics Letters* 122, 101104 (2023).

[2] D. Repp, et al., *Opt. Express* 31, 3364-3378 (2023).

[3] A. Fedotova, et al., *Photon. Res.* 11, 252-259 (2023).

[4] M. Weißflog, et al., *Laser & Photonics Reviews* 2200183 (2022).

[5] A. Kuppadakkath, et al., *Nanophotonics*, DOI: 10.1515/nanoph-2022-0235 (2022).

[6] M. Moradi, et al., *Nanoscale* DOI: 10.1039/d2nr02654f (2022).

[7] S. Saravi, et al., *Frontiers Photonics* DOI: 10.3389/fphot.2022.953105 (2022).

[8] A. Barreda, et al., *Journal of Quantitative Spectroscopy and Radiative Transfer* 276, 107900 (2021).

[9] T. Santiago-Cruz, et al., *Nano Lett.* 21, 4423-4429 (2021).

[10] A. Vaskin, et al., *Opt. Express* 29, 5567-5579 (2021).

[11] F. Löchner, et al., *ACS Photonics* 8, 218-227 (2021).

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Thomas Pertsch^{1,2,3}

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[6] M. Moradi, et al., *Nanoscale* DOI: 10.1039/d2nr02654f (2022).

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Optimizing the synthesis of gold nanotriangles and their potential in LSPR sensing

Ekaterina Podlesnaia, Princess Gerald Inangha, James Vesenka, Buşra Çinçin, Martin Seyring, Hans-Jürgen Hempel, Markus Rettenmayr, Andrea Csáki, and Wolfgang Fritzsche

Leibniz Institute of Photonic Technology, Albert-Einstein-Straße 9, 07745 Jena, Germany

The synthesis of plasmonic nanoparticles has drawn great attention in the last decades. The study of crystal growth mechanisms and optimization of the existing techniques lead to the increasing accessibility of nanomaterials, which have a high potential in the fields of plasmonics and catalysis [1-6]. However, promising shape-anisotropic structures are not thermodynamically favorable and can be only derived following fine and laborious procedures the mechanisms of which have not been studied thoroughly yet [7-9]. We examined the existing seed-mediated synthesis of gold nanotriangles [10] with UV–VIS time-resolved measurements. Tracing the particle evolution allowed for defining the critical time points for each step and reducing the time consumption from three days to one only without a loss in final product quality [11]. Next, we develop the synthesis utilizing a continuous microfluidic setup, which provides a highly efficient mixing and simple parameter control [12]. We show that the crystallinity of primary seeds is determined by the type of the implemented reactor, which further influences the shape yield [13]. The use of microfluidic seeds leads to the formation of well-defined triangles with narrower size distribution compared to the entirely conventional batch synthesis. These studies allow us to design an automatized platform for micro-continuous flow synthesis. Together with thorough parameter optimization, it will bring a new potential in streamlining and scaling up nanomaterial production, which in turn would provide a cost reduction in sensor fabrication.

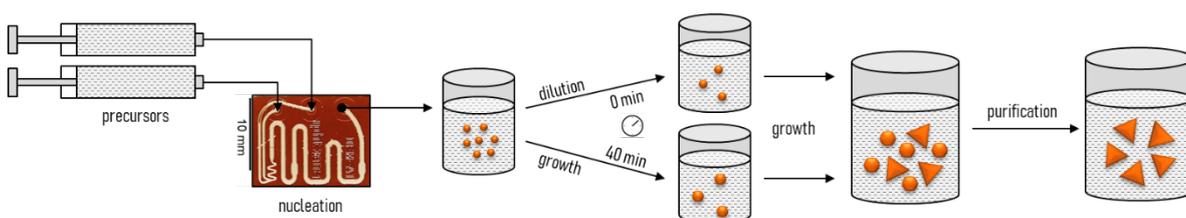


Fig. 1: The representation of gold nanotriangle synthesis implementing a microfluidic setup

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- [9] Scarabelli, L., et al., *ACS Nano* 2014, 8 (6), 5833-5842.
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- [11] Podlesnaia, E., et al., *Nanomaterials* 2021, 11 (4).
- [12] Thiele, M., et al., *Lab on a Chip* 2017, 17 (8), 1487-1495.
- [13] Podlesnaia, E., et al., *Small* 2023, 2204810.

Plasmons for sensors implanted under the skin

Katja Buder, Katharina Käfer, Bastian Flietel, Celiksoy, S., Thies Schröder, Carsten Sönnichsen*

Department of Chemistry, Johannes Gutenberg University of Mainz, Germany

Macroporous hydrogels are an attractive platform for implantable sensors because the network of interconnected macropores facilitates tissue integration. Embedded sensing elements, in our case plasmonic gold nanoparticles, can transduce the presence, absence and concentration of biochemical markers to the outside [1]. We discuss how to integrate such nanosensors into a macroporous hydrogel while preserving nanosensor functionality, in order to produce implantable sensors. We demonstrate that out of four different polymers, a poly(2-hydroxyethyl methacrylate)-poly(ethylene glycol)diacrylate-copolymer (pHEMA-PEGDA) results in a working sensor [2]. Our approach of incorporating nano-sized sensor elements into a hydrogel matrix generally identifies suitable polymers for implantable sensor systems. We test the implants by detecting the presence and concentration of a drug (Kanamycin) in the blood of hairless rats.

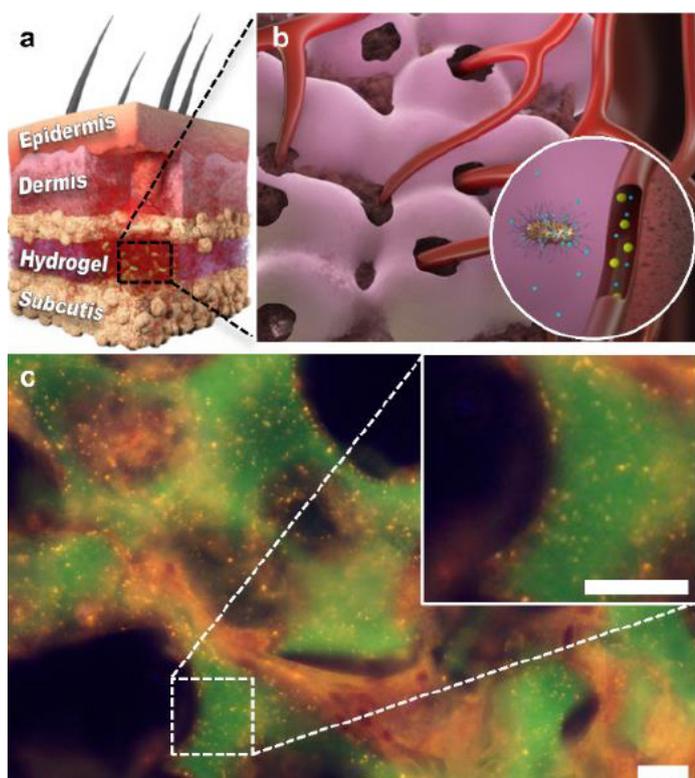


Fig. 1: The macroporous hydrogel implant. (a) Cross section of skin showing different layers and the hydrogel implant in the subcutaneous tissue. (b) Schematic of the hydrogel structure with embedded gold nanosensors. Tissue (brown) and blood vessels grow into the interconnected macropores facilitating analyte transport deep into the implant. The inset shows how small molecules (turquoise) diffuse to the nanosensors embedded in the hydrogel (pink). The hydrogel prevents larger molecules such as proteins (yellow) from reaching the sensors. (c) Dark-field image of a well-integrated hydrogel (histological section). Tissue (orange) has grown into the scaffold's macropores. The plasmonic nanosensors (small red dots) are visible inside the hydrogel matrix which appears green. The inset shows a magnified view of the evenly dispersed particles inside the gel. Scale bars are 20 µm.

[1] Käfer, K.; Buder, K (Krüger, K)*.; Schlapp, F.; Uzun, H.; Celiksoy, S.; Flietel, B.; Heimann, A.; Schröder, T.; Kempfski, O.; Sönnichsen, C. *Nano Letters* 21 (2021) 3325 (* maiden name)

[2] Buder, K.; Käfer, K.; Flietel, B.; Uzun, H.; Schröder, T.; Sönnichsen, C. *ACS Applied Bio Materials* 5 (2022) 465–470.

Plasmonic biosensor for cytokine detection in single immune cells

Eiichi Tamiya^{1,2} Jessiel Gueriba¹ Masato Saito² Hidenori Nagai¹
National Institute of Advanced Industrial Science and Technology¹, Osaka University²
2-1 Yamadaoka, Suita, Osaka, Japan

Cytokines are a class of secreted proteins involved in a variety of biological events, including immune responses, haematopoiesis and acute phase reactions. They have also been implicated in cytokine storms and serious diseases such as infections and cancer. Immune cells are heterogeneous cell populations with multiple types of prevailing activity, and the development of methods for the detection of cytokines at the single-cell level is thought to contribute to the elucidation of the causes of disease and the development of new therapeutic strategies. Here, we focus on biosensors that use localized surface plasmon resonance (LSPR) for real-time and label-free detection. We have developed a gold-capped nanopillar LSPR biosensor that can be mass-produced using nanoimprint technology (1). However, the detection sensitivity of conventional LSPR-based biosensors is not sensitive enough to detect secreted proteins at the single cell level. In this study, therefore, to improve the sensitivity by utilizing the hotspot effect, cauliflower-like nanostructures were fabricated on the LSPR sensor chip and microwell chips for single-cell capture were fabricated. The simple integration of these two chips demonstrated and validated a biosensor for the detection of single-cell-level secretions by IL-6-overexpressing cells. Fig.1(a) shows a schematic diagram of the single-cell-level secretion-detecting biosensor. The cauliflower-shaped nanostructured LSPR biosensor (Fig.1(b)) was fabricated by applying oxygen plasma etching to cyclo-olefin polymer (COP)-based nanopillars fabricated by nanoimprinting technology (2). This small uneven structure formed on the surface of the nanopillars results in more hotspot effects and improves sensing sensitivity. Cell capture chips with microchamber structures were also fabricated by nanoimprinting (3). In this experiment, single cell trapping was performed by fabricating microchambers with a diameter of 15 μm and a depth of 20 μm , as the diameter of Jurkat cells is 8-12 μm . After confirming single cell trapping under a microchamber, an anti-IL-6 modified LSPR sensor chip was placed on top of the cell trapping chip and used as a cover. LSPR spectral data from cells were measured over time and peak wavelengths are shown in Fig.1(c) IL-6 from single Jurkat cell could be monitored by red shift of the spectrum by the spectral imaging system. The results indicate that this LSPR biosensor device is capable for single-cell level IL-6 secretion detection and shows the potential to conduct real-time monitoring of cell secretion which would greatly help us to identify the viability and biological variation of the target cell.

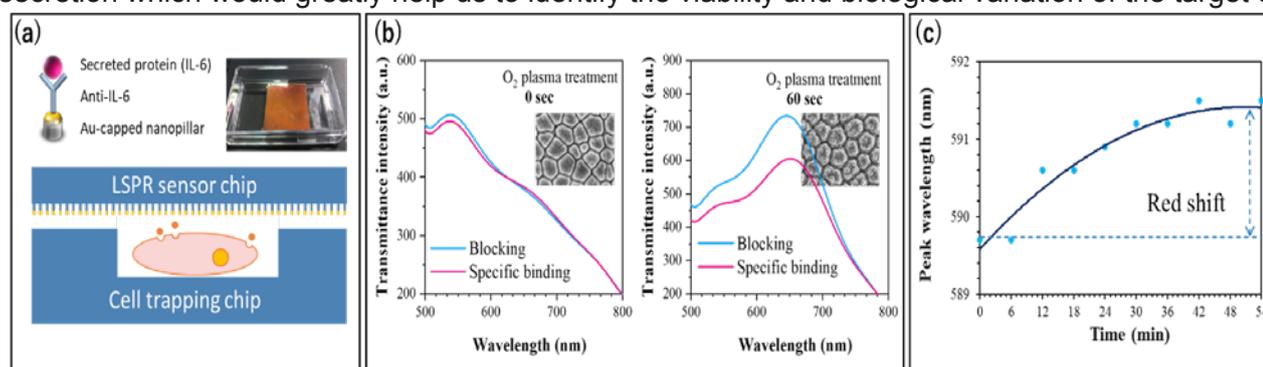


Figure 1. (a) Schematic image of the single-cell level secretion biosensor. (b) Sensing sensitivity improvement by oxygen plasma etching. (c) Monitoring of single cell secretion.

- 1) M. Saito, et al. *Anal. Chem.* **2012**, *84*, 5494–5500
- 2) C. Zhu, et al. *Micromachines*, **2020**, *11* (1), 107
- 3) X. Luo, et al. *Bull. Chem. Soc. Jpn.* **2020**, *93*, 1121–1126

Ultra-fast photochemistry in the strong light-matter coupling regime

Arpan Dutta, Ville Tiainen, Luis Duarte, Nemanja Markešević, Dmitry Morozov, Ruth Tichauer, Hassan A. Qureshi, Gerrit Groenhof, [Jussi Toppari](#)

Nanoscience Center & Departments of Physics and Chemistry, 40014 University of Jyväskylä, Finland

Strong coupling between photoactive molecules and confined light modes, such as, surface plasmons or photons in optical cavities, results in the formation of hybrid light-matter states ‘polaritons’ with energies above and below the original state [1]. Such modification of the excited state can alter the photo-chemical behavior of the molecule.

Here we investigate the influence of strong light-matter coupling on an ultrafast photochemical reaction, *i.e.*, the excited-state intramolecular proton transfer (ESIPT), of 10-hydroxybenzo[h]quinoline (HBQ). The reaction starts when HBQ is excited by ultraviolet light around 375 nm, and after the proton transfer the molecule radiatively decays back to the ground state by emitting around 620 nm, which we use as a measure of the reaction efficiency. To obtain the strong light-matter coupling with varying coupling strengths, we embedded different concentrations of HBQ within metallic Fabry-Perot cavities tuned to have the first order cavity mode in resonance with the HBQ excited state, as shown in figure 1a. The change in the potential energy surface due to polariton formation would suggest increase of the reaction barrier with increased coupling and thus hindering of the ESIPT. However, our experiments show enhanced emission yield [2] with increasing coupling.

More detailed excitation spectroscopy reveals that the excitation spectrum under strong coupling is a convolution of the excitation spectrum of the “bare” molecules and the absorption spectrum of the molecule-cavity system. The results of our experiments and simulations suggest that rather than suppressing the reactivity, polaritons can act as gateways to efficiently channel excitations into molecules, which can then react “normally”. On the other words, upon excitation of a polariton state, the excitation energy localizes onto a HBQ molecule which undergoes ESIPT, as depicted in figure 1b. Furthermore, this process seems to be fully independent of the type and nature of the excited polariton state and only depends on the spectral overlap between the polariton and the molecular dark states [3]. Since this overlap is increasing with increased HBQ concentration, we see enhancement of ESIPT as a function of the coupling strength. Our findings are important in the context of polaritonic chemistry, where influencing photochemical reactions via strong light-matter coupling is crucial.

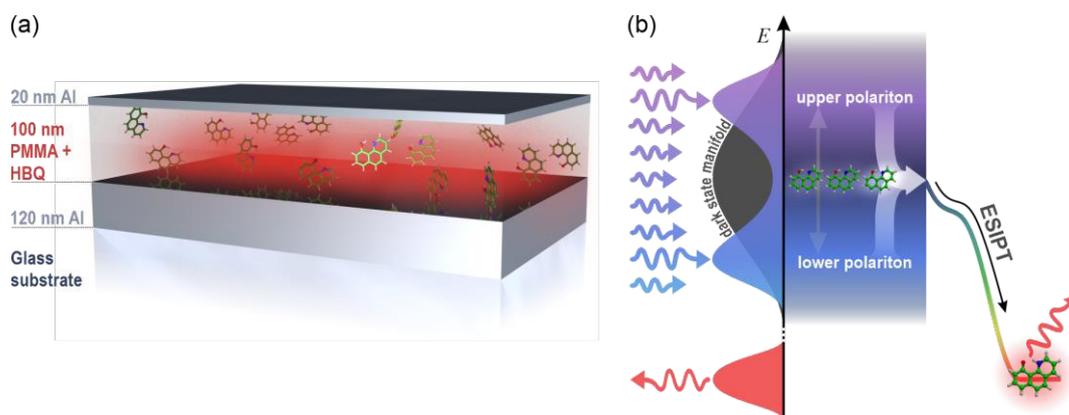


Fig. 1: (a) Schematic of the utilized cavity geometry with HBQ molecule inside.
(b) Schematic presentation of ESIPT in HBQ with excitation energy channeled via polaritons.

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Dual-Light responsive tuning of dielectric metasurface based on molecular photoswitches

Sarah L. Walden¹, Purushottam Poudel², Felix H. Schacher², Isabelle Staude¹

¹Institute for Solid State Physics, Abbe Center of Photonics, Friedrich-Schiller-University Jena

²Institute of Organic Chemistry and Macromolecular Chemistry (IOMC), Friedrich-Schiller-University Jena

Light is an attractive stimulus to tune the optical response of dielectric metasurfaces, and it is mild, allows high spatio-temporal control and possess a high degree of variability, based on the choice of wavelength. Recently, we demonstrated that hybridization of a dielectric metasurface with a dual light- and temperature-responsive copolymer segment consisting of photo-responsive azobenzene (AZO) and temperature-responsive triethylene glycol acrylate (TEGA) allows tuning of the dielectric metasurface resonance frequencies using light, temperature, or a combination of both as external stimuli [1].

Here we present high-quality factor Si metasurfaces with optical resonance in the near-infrared wavelengths, that are subsequently coated with photoresponsive polymers. The spatial photo-tunability of the metasurface has been investigated using two different light-responsive polymers shown in Fig. 1, namely pAZO and pSPA, hosting azobenzene and spiropyran photoswitches, respectively, as pendent groups. The switching of the pAZO and pSPA polymers induces a refractive index change around the metasurface causing a blue- and red-shift in the resonant wavelength of the metasurface, respectively.

Owing to the different absorption spectra of the photoswitches, step-wise, light-mediated and reversible, switching of the individual polymers can be achieved by simply applying different colors of light. By spatially patterning the polymers on the metasurface array, spatial modulation of the metasurface resonance is achieved.

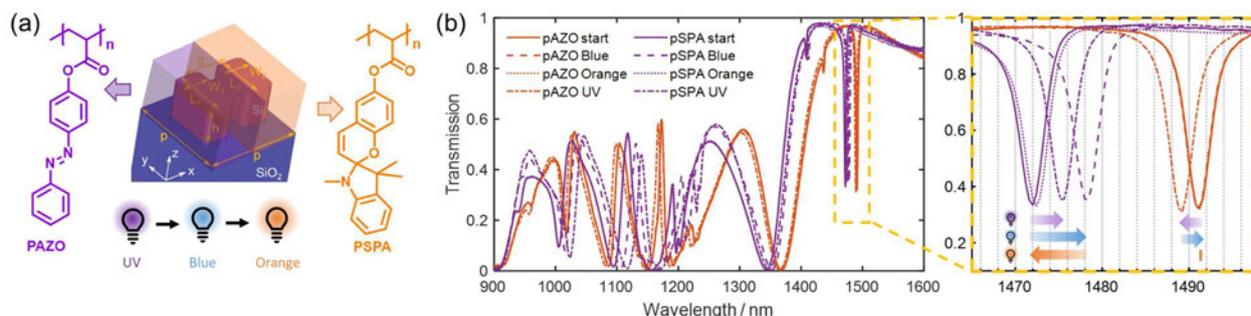


Fig. 1: (a) Chemical structures of pAZO and pSPA and schematic representation of metasurface. (b) Measured multi-light responsive tunable transmittance of the metasurface covered with spatially offset pAZO and pSPA by applying different wavelengths of light.

[1] Zou, C., et al., *Adv. Optical Mater.* 11, 2202187, 2023

Deep-UV autofluorescence detection of single proteins using nanophotonics

Prithu Roy, Jean-Benoit Claude, Jerome Wenger

Aix Marseille Univ, CNRS, Centrale Marseille, Institut Fresnel, AMUTech, 13013, Marseille, France

The ability to detect and study individual proteins in their natural state without the use of fluorescent labels is crucial for gaining a deeper understanding of their behavior and function in their native environment. However, the contemporary technique of fluorescence labeling can modify the structure and function of proteins, thereby compromising the accuracy of information gathered about their behavior in vivo. Although the natural UV autofluorescence of proteins is a potential solution (with excitation at 250-290 nm and emission at 320-360 nm), the low quantum yield and absorption cross-section of the emitters in UV presents a challenge.

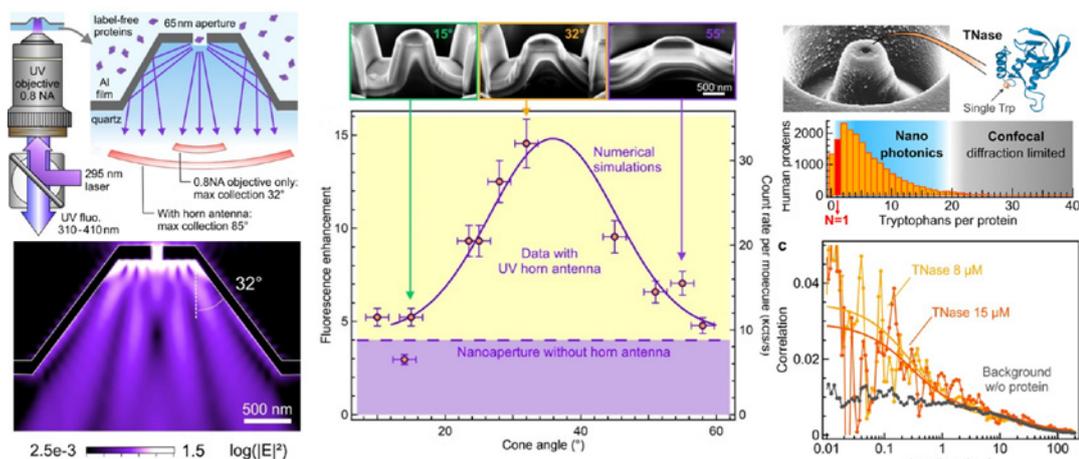


Fig. 1 The optical horn antenna concept, simulation, experimental data and its application in protein sensing

To address this challenge, we have developed a new optical horn antenna platform for label-free detection of individual proteins in the ultraviolet (UV) range with unprecedented resolutions and sensitivity[1]. Our approach involves combining a conical horn reflector for fluorescence collection at ultrahigh angles with a metal nanoaperture for fluorescence enhancement and background screening. The horn antenna increases the signal from proteins by more than an order of magnitude. Building on the success of the optical horn antenna platform, we pushed the sensitivity to detect down to the single tryptophan level[2]. By using plasmonic antennas, antioxidants, and background noise reduction techniques, we were able to improve the signal-to-background ratio by over an order of magnitude. This enabled the use of UV-fluorescence correlation spectroscopy (UV-FCS) on proteins with a single tryptophan by simultaneously enhancing plasmonic fluorescence, collecting fluorescence efficiently, detecting attoliter volumes, strongly rejecting background noise, and achieving high signal-to-noise ratios (SNRs). This unprecedentedly brightens the detected UV photon count rate, which is critical for investigating single proteins in their natural state in real-time. By combining these techniques, we were able to achieve single-molecule single-emitter sensitivity, a significant breakthrough that opens up the possibility of applying the UV-FCS technique to a vast library of label-free proteins.

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POSTER PRESENTATIONS

Modulating the Temporal Dynamics of Nonlinear Ultrafast Plasmon Resonances // Hira Asif (Antalya)

DNA origami based plasmonic nanoantennas for SERS – transition from few-molecule to single molecule detection // Ilko Bald (Potsdam)

Influence of metal nanoparticle size on plasmon-induced reactions // Christina Beresowski (Potsdam)

Broadband Four-Wave Mixing Enhanced by Plasmonic Surface Lattice Resonance and Localized Surface Plasmon Resonance in an Azimuthally Chirped Grating // Abhik Chakraborty (Jena)

Monitoring plasmon-mediated chemical reactions on immobilized noble metal nanoparticle // Lars Dannenberg (Berlin)

Dielectric Loaded Plasmonics for Active Tuning of Spin-Orbit Coupled Surface Plasmon Polaritons // Abhrodeep Dey (Jena)

Raman-based detection of natural products in microbial communication // Tony Dip (Jena)

Exploring the sensitivity and reproducibility of electrochemically assisted SERS using silver nanostructures // Aradhana Dwivedi (Jena)

Point-of-care Raman microspectroscopy for detecting head and neck tumour markers in body liquids // Edoardo Farnesi (Jena)

Composition-Dependent Liposome Structure as Revealed by Surface-Enhanced Raman Scattering and Cryo-Electron Microscopy // Yiqing Feng (Berlin)

Conformational Dynamics of a Single Protein // Bastian Flietel (Mainz)

Hot Electron Mediated Plasmonic Catalysis monitored by Surface- Enhanced Raman Spectroscopy employing Ag Nanorods Array // Shashank K. Gahlaut (Potsdam)

Photonic and plasmonic resonators with topological properties for sensitive sensing and quantum applications // Manuel Gonçalves (Ulm)

Aptamer-functionalized gold nanoparticles for the highly-sensitive dual-detection of C-reactive protein // Alexandru-Milentie Hada (Cluj-Napoca)

Rotavirus-proteins affinity dynamics via surface plasmon resonance biosensor // César Herreño (Bogota)

Plasmonic Surface Lattice Resonances in Arrays of Gold Nanoparticles // César Herreño (Bogota)

Near Infrared Plasmonic & reduced Graphene Oxide Hybrid Nanoplatfrom for Photothermal Therapy // Alexandru Holca (Cluj-Napoca)

Monitoring Photolipid Bilayer Membrane Switching with Plasmonic Nanorods // Dominik Kammerer (Munich)

Investigating ligand binding to G-quadruplex DNA at the single-molecule level via plasmon-enhanced fluorescence // Ashish Kar (Leuven)

Plasmon-enhanced diffractive supercells // Hamid Keshmiri (Berlin)

Gold Nanorod DNA Origami Antennas for 3 Orders of Magnitude Fluorescence Enhancement in NIR // Karol Kolář (Fribourg)

NanoSPR for Biological Sensing // Alena Kuzmina (Mainz)

Plasmonic bound states in the continuum for strong light-matter interaction // Yao Liang (Hong Kong)

Raman-based Detection of Antibiotics and Metabolites in Pharmaceutical Formulations and Clinical-relevant Matrices // Chen Liu (Jena)

Characterization of the sensing potential of assembled plasmonic nanostructures // Yeshni Luximun (Jena)

Development of EVs Detection Device Based on AC Electroosmosis // Ibuki Machi (Kure)

Large $Ti_3C_2T_x$ MXene dimers as SERS substrates // Hayk Minassian (Yerevan)

Towards modulating near-field plasmonic coupling for enhanced optical spectroscopy // Dario Cattozzo Mor (Prague)

Mathematical model to predict the cellular internalization of gold nanoparticles // Orlando Narv ez Gonz alez (Bogota)

Insulator-based Dielectrophoresis Device Utilizing Positive Dielectrophoresis for Dielectric Characteristics Measurement // Koki Nietani (Kure)

Aiming for metasurfaces by DNA-assisted lithography // Johannes Parikka (Jyv skyl )

Nanoantenna Conjugated Graphene Photodetector // Abhinav Raina (Cologne)

Optimizing Photothermal Therapy for Cancer Treatment using Scuff-EM and K-Wave Simulations // Angelo Abraham Sanz (Bogota)

Bi-metallic and nano-porous particles fabricated by pulsed UV laser irradiation for plasmonic sensing // Gabriele Schmidl (Jena)

Ultrafast spatiotemporal chiroptical response of dielectric and plasmonic nanoparticles // Ankit Kumar Singh (Jena)

SERS probing of endolysosomes with gold nanostars // Cecilia Spedalieri (Berlin)

Optical waveguide (OW) biosensor // Keiji Tada (Nishinomiya)

Near-Infrared Luminescent Platinum Nanoclusters for in vivo Imaging and Biomedical Application // Shin-ichi Tanaka (Kure)

On the Road from Top-down to Bottom-up by DNA-Assisted Lithography // Kosti Tapio (Jyv skyl )

Controlling the selective adsorption of plasmonic DNA origami nanostructures using polar surface arrays // Zunhao Wang (Braunschweig)

Meta-devices for 6G applications and beyond // Jing Cheng Zhang (Hong Kong)

Monitoring Photolipid Bilayer Membrane Switching with Plasmonic Nanorods // Jinhua Zhang (Munich)

Modulating the temporal dynamics of nonlinear ultrafast plasmon resonances

Hira Asif, Ramazan Sahin

Faculty of Science, Department of Physics, Akdeniz University Antalya, Turkey

We propose the lifetime enhancement of second harmonic (SH) plasmon mode in Au nanoparticle by coupling it with a two-level quantum emitter. Under two-coupled harmonic oscillator model, we compute the time-dependent response of SH mode supported by Au nanoparticle (AuNP) coupled with a two-level quantum emitter (QE). We evaluate the lifetime enhancement factor as a function of coupling strength and tuned resonant frequencies. The results show that tiny object like QE with sharp spectral bandwidth, small decay rate, and large oscillating strength is more efficient to control and probe the temporal dynamics of the SH field, as compared to DM which have a wide spectral bandwidth. We propose the lifetime enhancement of the second harmonic (SH) plasmon mode exclusively after the natural decay time of the fundamental mode (FM), which distinguishes SH mode irrespective of its spatial convolution with elementary modes. Our proposed AuNP-QE coupled plasmonic system supporting nonlinear signal with enhanced temporal character paves its way for designing efficient on-chip nonlinear optical devices and can be a powerful tool in ultrahigh resolution nonlinear optical imaging.

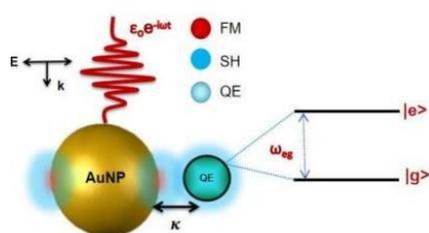


Fig. 1

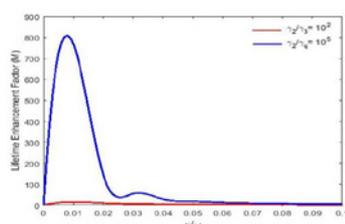


Fig. 2

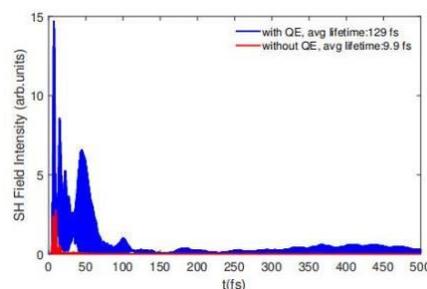


Fig. 3

Fig. 1: AuNP-QE coupled system.

Fig. 2: Lifetime enhancement factor for two different decay rates ratios

Fig. 3: SH field intensity as a function of time

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DNA origami based plasmonic nanoantennas for SERS – transition from few-molecule to single molecule detection

[Ilko Bald](#), [Yuya Kanehira](#), [Amr Mostafa](#), [Anushree Dutta](#), [Sergio Kogikoski Jr.](#)

[University of Potsdam, Karl-Liebknecht-Straße 24-25, 14476 Potsdam, Germany](#)

DNA origami nanostructures are ideally suited to arrange both plasmonic nanoparticles as well as receptors for analyte molecules with nanometer precision. Thus, they can be exploited for surface-enhanced Raman scattering (SERS), where the strongest signal enhancement is localized in nanometric hot spots and where the DNA origami can be used to precisely position the molecules of interest. In recent years we have demonstrated the few- and single-molecule SERS detection in different nanoparticle arrangements.[1]-[4] We have created a dedicated DNA origami nanoantenna,[4] which was also used to study chemical changes in hemin,[5] and to detect single proteins.[4]

In the present contribution we demonstrate the further optimization of the nanoantenna by comparing the SERS performance of dimers of different nanoparticle species from spherical Au and Ag nanoparticles to anisotropic gold nanoflowers and combinations thereof. A combination of Au nanoflower and Ag nanosphere allows for a broadband SERS excitation and improved single-molecule detection.

With these structures at hand we studied systematically how SERS spectra are modified when transitioning from bulk spectra over few molecules up to the single molecule level. Latest measurements from small molecules as well as proteins will be shown.

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[5] A. Dutta et al., *Nanoscale* **2022**, 14, 16467.

Influence of metal nanoparticle size on plasmon-induced reactions

Christina Beresowski, Sergio Kogikoski, Ilko Bald

Institute of Chemistry, University of Potsdam, Karl-Liebknecht-Straße 24-25, 14476 Potsdam
Germany

Hot charge carriers are generated through the non-radiative decay of localised surface plasmon resonances in noble metal nanoparticles. They can induce chemical reactions of molecules adsorbed to the plasmonic nanoparticles.¹ To understand the influence of nanoparticle size on the hot electrons-induced reactions, we studied the decomposition of 8-Bromoadenine (BrAde) forming Adenine (Ade) adsorbed on different sized Au- and Ag nanoparticle aggregates by surface enhanced Raman spectroscopy (SERS). By using the decay curve of the ring breathing mode of BrAde the reaction rate was calculated and compared for each size.

The results show a clear increase in the decomposition reaction rate as the Au- and Ag nanoparticle diameter increased in diameter. The main reason for that increase is the larger absorption cross section of larger diameter nanoparticles.² Further insight is gained through the analysis of the rate in function of the laser wavelength, where the reaction at 532 nm is faster than at 633 nm and 785 nm.³

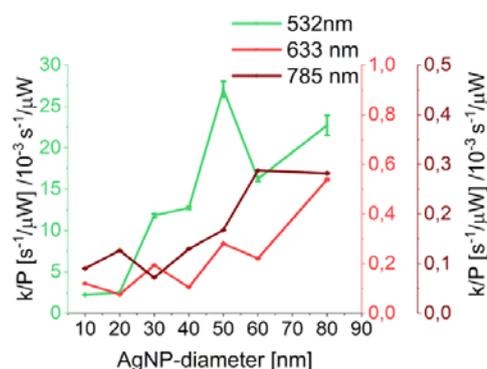
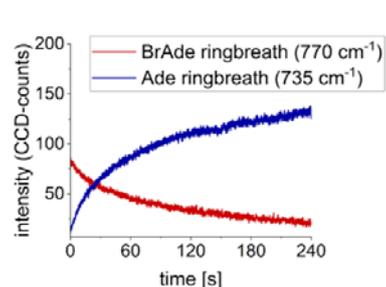
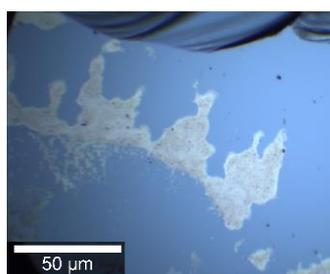


Fig. 1

Fig. 2

Fig. 3

Fig. 1: Brightfield microscopic image of the aggregated AgNPs (40nm) capped with BrAde.

Fig. 2: Kinetic plot of BrAde decomposition at 770 cm^{-1} (red) and Ade formation at 735 cm^{-1} (blue) as a function of the illumination time on 40 nm AgNPs.

Fig. 3: Plot of the calculated reaction rate (k) normalised by the used Laser power for different AgNP diameter sizes and different laser wavelengths.

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Broadband Four-Wave Mixing Enhanced by Plasmonic Surface Lattice Resonance and Localized Surface Plasmon Resonance in an Azimuthally Chirped Grating

Abhik Chakraborty,^{1,2} Parijat Barman,^{1,2} Ankit Kumar Singh,² Xiaofei Wu,² Denis A. Akimov,² Tobias Meyer-Zedler,^{1,2} Stefan Nolte,^{3,4} Carsten Ronning,⁵ Michael Schmitt,¹ Jürgen Popp,^{1,2} Jer-Shing Huang^{1,2,6,7}

¹Institute of Physical Chemistry and Abbe Center of Photonics, Friedrich-Schiller-Universität Jena, Helmholtzweg 4, D-07743 Jena, Germany

²Leibniz Institute of Photonic Technology, Albert-Einstein Str. 9, 07745 Jena, Germany

³Institute of Applied Physics, Abbe Center of Photonics, Friedrich-Schiller-Universität Jena, Albert-Einstein-Straße 15, Jena 07745, Germany

⁴Fraunhofer Institute for Applied Optics and Precision Engineering IOF, Center of Excellence in Photonics, Albert-Einstein-Str. 7, Jena 07745, Germany

⁵Institut für Festkörperphysik, Friedrich-Schiller-Universität Jena, Max-Wien-Platz 1, 07743 Jena, Germany

⁶Research Center for Applied Sciences, Academia Sinica, 128 Sec. 2, Academia Road, Nankang District, Taipei 11529, Taiwan

⁷Department of Electrophysics, National Yang Ming Chiao Tung University, Hsinchu 30010, Taiwan

With the rational optimization of a plasmonic azimuthally chirped grating (ACG), we report the generation and enhancement of broadband four-wave mixing (FWM). The FWM signal originates from the instantaneously polarized electronic resonances inherent in matter.^[1] However, the enhancement of said signal depends on the resonant enhancement enforced by the cavity.^[1] The ACG provides a continuously varying grating periodicity which, in turn, offers the necessary phase-matching conditions capable of mediating the near field and the far field over a broad range of wavelengths.^[1,2,3] In addition to that, the V-shaped grating grooves individually act as hosts of plasmonic hot spots, thereby, facilitating frequency conversion and field enhancement by virtue of their broad momentum distribution and mode confining capabilities.^[1] This work sheds light on the interplay between the groove geometry-dependent localized surface plasmon resonance (LSPR) and the periodicity-dependent plasmonic surface lattice resonance (PSLR) to conclusively demonstrate and explicate the generation and enhancement of broadband FWM in an ACG.

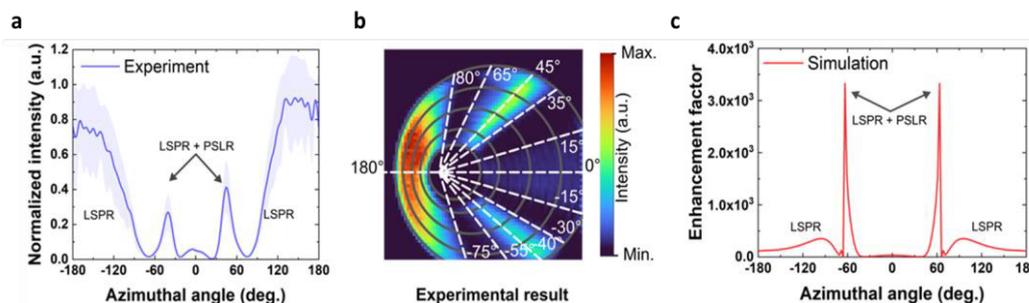


Fig. 1: (a, b) Experimentally observed normalized broadband FWM intensity and (c) simulated broadband FWM intensity enhancement factor in the ACG at $\lambda_{\text{FWM}} = 747$ nm.

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Monitoring plasmon-mediated chemical reactions on immobilized noble metal nanoparticles

[Lars Dannenberg](#), [Janina Kneipp](#)

[Humboldt-Universität zu Berlin, Brook-Taylor-Straße 2, 12489 Berlin, Germany](#)

The educts and/or products of plasmon-assisted reactions can be studied by sensitive spectroscopy, as plasmonic nanostructures can be used to enhance a chemical reaction and at the same time provide high local fields for surface-enhanced Raman scattering (SERS). The choice of plasmonic structures to catalyze a chemical reaction and to characterize them precisely plays an important role in elucidating the physical processes and the chemical mechanisms. Well-known reactions, such as the conversion of 4-aminophenol to 4,4'-dimercaptoazobenzene, demonstrate the potential of plasmonic catalysis.^[1] but the role of localized surface plasmon resonances (LSPR) in many other organic transformations is not understood and can be studied by SERS. The use of nanoparticle solutions may have disadvantages with respect to Brownian motion of the plasmonic substrate and stability in the presence of reaction products. By the immobilization of nanoparticles on a functionalized surface, the plasmon-mediated reaction can be observed in a shorter or longer time interval on the surface without the nanostructures of interest moving out of the focal volume, and also spatially resolved data (and reaction control) can be obtained.^[2] In addition, a well-defined and characterized surface with immobilized particles can lead to better reproducible results compared to measurements in solution. The immobilization of the nanoparticles in combination with well-chosen plasmon-assisted reactions can lead to new and efficiently fabricated materials.

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Dielectric Loaded Plasmonics for Active Tuning of Spin-Orbit Coupled Surface Plasmon Polaritons

Abhrodeep Dey, Ankit Kumar Singh, and Jer-Shing Huang

Leibniz Institute of Photonic Technology, Albert-Einstein-Straße 9, 07745 Jena, Germany

Dedicated optimization of plasmonic geometries in the nanoscale can be employed to efficiently host strongly localized electromagnetic modes in the near field via the satisfaction of momentum-matching condition. The refractive index contrast at the interface, that is pivotal to attain strongly localized mode confinement, can be tailored by employing appropriate dielectric-loaded plasmonic system. In this work, we propose such a system that comprises of a dielectric grating on top of a thin gold film using a phase change material (PCM) known as Stibnite (Sb_2S_3). The usage of PCMs provides useful advantage of drastic optical property change once tuned from their amorphous to crystalline state [1]. Sb_2S_3 can be easily tuned from amorphous to crystalline state at an ultrafast rate using an optical beam [1, 2]. The dielectric grating (Fig. 1) is designed to exhibit a circular polarization-dependent directional coupling [3]. Finite-difference time-domain (FDTD) simulations based on amorphous Sb_2S_3 fishbone grating exhibit strong directional propagation of SPP, the directionality of which changes when the handedness of circular polarization is changed. Interestingly, when the phase is switched to crystalline Sb_2S_3 , the aforementioned handedness-dependent response remains but the directionality gets reduced (Fig. 2) from 7.78 dB (amorphous) to 2.5 dB (crystalline). Furthermore, using the same principle, we also demonstrate a focusing/defocusing of the coupled SPPs depending on the handedness of the circular polarization of incident light (as shown in Fig. 3 and 4).

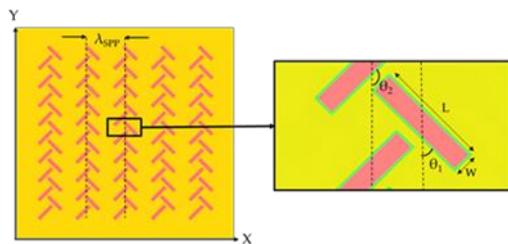


Fig. 1

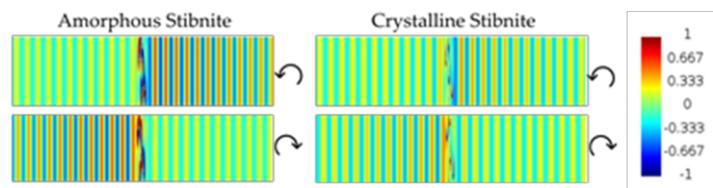


Fig. 2



Fig. 3

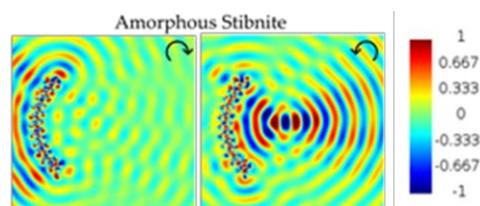


Fig. 4

Fig. 1: The proposed dielectric loaded fishbone structure

Fig. 2: FDTD simulations of directional E-field distribution ($E_{\text{out}}/E_{\text{in}}$) of coupled SPPs based on the handedness of circularly polarized light (CPL). The circular arrows indicate the polarization of light in either case

Fig. 3: quarter Arc fishbone structure

Fig. 4: FDTD simulations of E-field distribution in amorphous Stibnite Quarter Arc fishbone under Right CPL (left) and Left CPL (right)

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Raman-based detection of natural products in microbial communication

Tony Düb^{1,3}, Simone Edenhart^{2,4}, Dana Cialla-May^{1,3}, Jer-Shing Huang^{1,3}, Axel A. Brakhage^{2,4}, Juergen Popp^{1,3}

¹ Leibniz Institute of Photonic Technology, Member of Leibniz Health Technologies, Member of the Leibniz Centre for Photonics in Infection Research (LPI), Jena, Germany

² Leibniz Institute for Natural Product Research and Infection Biology (Leibniz-HKI), Jena, Germany

³ Institute of Physical Chemistry (IPC) and Abbe Center of Photonics (ACP), Friedrich Schiller University Jena, Member of the Leibniz Centre for Photonics in Infection Research (LPI), Jena, Germany

⁴ Institute of Microbiology, Friedrich Schiller University Jena, Jena, Germany

The interaction between the bacterium *Streptomyces rapamycinicus* or *S. iranensis* and the fungus *Aspergillus nidulans* triggers the activation of the silent fungal natural product biosynthesis genes, in particular of the orsellinic acid gene cluster. This leads to the production of orsellinic acid and derivatives thereof, like lecanoric acid and the F compounds F-9775A and F-9775B, whose ecological function remains obscure [1-3]. Production of fumigermin in *Aspergillus fumigatus* is also triggered by *S. rapamycinicus*. It inhibits germination of spores of some streptomycetes [4]. The characterization and detection of natural products by surface-enhanced linear and nonlinear Raman spectroscopy is expected to shed light on how they are released and transported through the environment, and how they trigger responses in other microorganisms.

Linear and nonlinear Raman-based detection techniques, namely surface-enhanced Raman spectroscopy (SERS) and coherent anti-Stokes Raman spectroscopy (CARS) and a combination of both (SE-CARS) using specific plasmonic substrates [5]. In the first phase of experiments, Raman and SERS spectra of orsellinic and lecanoric acids were recorded to identify and assign marker modes as well as achieve their detection in trace concentrations. Moreover, first results on the characterization of a plasmonic array specifically designed for SE-CARS are presented.

Acknowledgement: Funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) under Germany's Excellence Strategy – EXC 2051 – Project-ID 390713860.

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Exploring the sensitivity and reproducibility of electrochemically assisted SERS using silver nanostructures

Aradhana Dwivedi^{1,3}, Juergen Popp^{1,2}, Vladimir Sivakov¹, Dana-Cialla May^{1,2}

¹ Leibniz Institute of Photonic Technology, Member of Leibniz Health Technologies, Member of the Leibniz Centre for Photonics in Infection Research (LPI), Jena, Germany

² Institute of Physical Chemistry (IPC) and Abbe Center of Photonics (ACP), Friedrich Schiller University Jena, Member of the Leibniz Centre for Photonics in Infection Research (LPI), Jena, Germany

Electrochemical surface-enhanced Raman spectroscopy (EC-SERS) couples the highly sensitive molecular fingerprint SERS technique with electrochemistry where the SERS-active sensing surface acts as a working electrode. The Raman signal can be further enhanced in EC-SERS compared to the standard SERS technique due to the potential dependent adsorption and enrichment of the analyte molecule to the SERS active sites. [1] EC-SERS provides the freedom to tune the surface charge of the substrate, which is very useful in detecting and selecting charged biological molecules from complex matrices.

In this study, we use Ag nanostructures grown on Si surfaces [2] as a SERS active working electrode. At the metal-semiconductor interface, an effective charge transfer between Si and Ag can be observed, which allows for an increased charge-transfer enhancement of the Raman signal. As a test molecule, we use 4-Mercaptobenzoic Acid (4-MBA) in order to study the EC-SERS performance. This molecule contains a thiol group, which is known to bind towards the Ag surface and facilitates an effective charge transfer. The comparison between normal SERS and EC-SERS will be illustrated.

Silver nanostructures were grown on p-type Si wafers by one-pot galvanic displacement [2,3] Si substrates were immersed in a solution containing silver precursor and hydrofluoric acid in the volume ratio of 1:1 at ambient conditions. Prior to their application in EC-SERS, the substrates were characterized by SEM, XPS, and UV-Vis spectroscopy. Finally, the substrates were immersed into the analyte solution, i.e. 4-MBA for the SERS measurements.

Acknowledgement: We gratefully acknowledge the DFG for funding projects CI344/3-1 and SI1893/30-1.

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Point-of-care Raman microspectroscopy for detecting head and neck tumour markers in body liquids

[Edoardo Farnesi](#), [Chen Liu](#), [Dana Cialla-May](#), [Michael Schmitt](#), [Juergen Popp](#)

[Leibniz Institute of Photonic Technology, Albert-Einstein-Straße 9, 07745 Jena, Germany](#)

Traditional methods for head and neck cancer diagnostics, which include clinical examination, white light endoscopy, radiological imaging, and fine-needle aspiration cytology, for example, may have a limited diagnostic accuracy. Gold standard for proof of malignancy is a histopathological examination of tissue biopsies. Taking into consideration that such investigations generally are performed when the tumor is already clinically obvious, and are not reliable for head and neck cancer screening, novel, non-invasive, rapid diagnostics, especially to detect early cancer in a point-of-care (POC) setting are warranted. The analysis of body liquids (urine, serum, sputum) by Raman spectroscopy offers great potential as non- or less invasive approach for a rapid screening of cancer markers in an early stage. Here, we report about the development of spectral acquisition protocols for Raman spectroscopic measurements of body fluids to detect head and neck cancer markers.

One crucial point in investigating body liquids via Raman spectroscopy is the development of appropriate sample preparation methods. Thus, to reach the aforementioned goals, we develop standardized sampling approaches leading to reproducible Raman analysis of body liquids. In order to enhance the intrinsic weak Raman signal, surface enhanced Raman spectroscopy (SERS) can be applied by employing powerful plasmonic-active nanostructured sensing surfaces.

The recorded Raman and SERS spectra of the body fluids (urine, serum, sputum) are dominated by the contribution of well-known medical target molecules as lysozyme, phenylalanine and triptophan in saliva or hypoxanthine, urea and xanthopterin in urine. The researched spectral acquisition protocols will be implemented in an automated POC measuring protocol. Further goals of this study are the development of custom-made chemometric data evaluation protocols, involving the most innovative and efficient machine learning algorithms. This will result in standard operating procedures (SOPs) for the POC Raman spectroscopic analysis of body fluids to detect tumour markers, leading to an improved personalized treatment of patients. Additionally, the potential for early cancer detection will be evaluated, even before the onset of symptoms, with just a few drops of body fluid.

Composition-Dependent Liposome Structure as Revealed by Surface-Enhanced Raman Scattering and Cryo-Electron Microscopy

Yiqing Feng^{‡#}, Zdravko Kochovski[§], Christoph Arenz[‡], Yan Lu[§], Janina Kneipp[‡]

[‡] Department of Chemistry, Humboldt-Universität zu Berlin, Brook-Taylor-Str. 2, 12489 Berlin, Germany

[#] Einstein Center of Catalysis (EC2/BIG-NSE), Technische Universität Berlin, Marchstr. 6-8, 10587 Berlin, Germany

[§] Department for Electrochemical Energy Storage, Helmholtz-Zentrum Berlin für Materialien und Energie, 14109 Berlin, Germany
Institute of Chemistry, University of Potsdam, 14467 Potsdam, Germany

Due to the great potential of surface-enhanced Raman scattering (SERS) as local vibrational probe of lipid-nanostructure interaction in lipid bilayers, it is important to characterize these interactions in detail. Ceramide, the simplest sphingolipid that acts as important structural component and regulator of biological function lacks a phosphocholine head group that is common to many lipids used in liposome models and that can efficiently interact with gold nanostructures.

SERS spectra of liposomes of a mixture of ceramide, phosphatidic acid, and phosphatidyl choline, as well as of pure ceramide and of the phospholipid mixture are reported. The different spectral groups reveal the diverse types of interaction of the gold nanoparticles with lipids via sphingosine, phosphate, choline head groups and the acyl chains. Vibrational bands related to the state of order of the membrane, and moreover to the amide function of the sphingosine head groups indicate that the gold nanoparticles interact with molecules involved in different intermolecular relations. Cryogenic electron microscopy shows the formation of bilayer liposomes in all preparations. Pure ceramide was found to also form a large variety of supramolecular, concentric stacked and dense packed lamellar, non-liposomal structures. The predominant interaction of the gold nanoparticles with these structures suggests that the structural features revealed in the SERS spectra of pure ceramide must be characteristic of non-liposomal aggregations.

The characterization of ceramide structure and interaction by SERS extend the studies of lipids in biophysical and biological models.

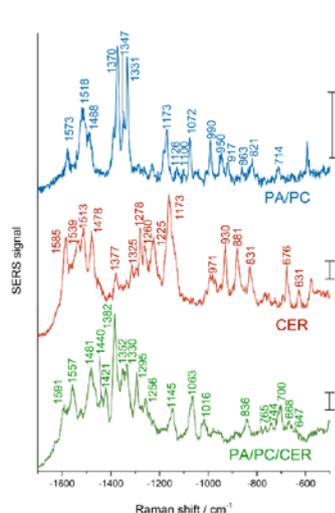


Fig. 1

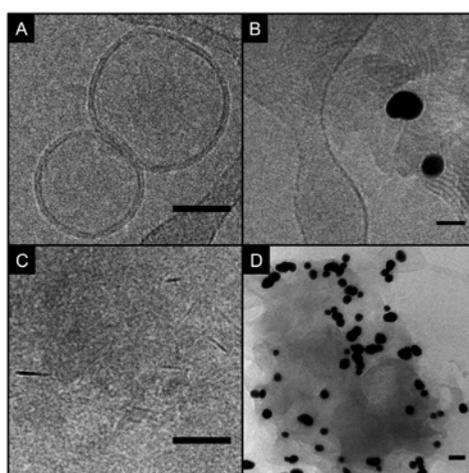


Fig. 2

Fig. 1: representative SERS spectra of gold nanoparticles and liposomes composed of phospholipid mixture (PA/PC), pure ceramide (CER) and the mixture of ceramide, phosphatidic acid, and phosphatidyl choline (PA/PC/CER)

Fig. 2: cryo-electron micrographs of pure ceramide preparation with gold nanoparticles

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Conformational Dynamics of a Single Protein Monitored for 24 Hours at Video Rate

[Bastian Flietel](#)¹, [Sirin Celiksoy](#)¹, [Thorsten Hugel](#)² and [Carsten Sönnichsen](#)¹

¹Department of Chemistry, University of Mainz, Duesbergweg 10-14, D-55128 Mainz, Germany

²Institute of Physical Chemistry, University of Freiburg, Albertstraße 23a, D-79104 Freiburg, Germany

Protein functions are determined by their structure and dynamics. Although the acquisition of structural information has been radically improved by advances in electron microscopy, it is difficult to obtain protein dynamics over a long period of time ^[1].

I present a new approach based on the single molecule plasmon ruler to study the conformation dynamics of a single protein at video rate for 24 hours in and out of equilibrium (i.e., without ATP). This method does not impose external forces on proteins and can measure the dynamics of proteins in several orders of magnitude, which not achievable by other single molecule techniques ^[2-5]. With this technique we explore the dynamics of the heat shock protein 90 (Hsp90) and identify states with long-term dwell times (related to rare visit states) in the minute timescale (along with the known fast dynamics in the 0.1 s to 10 s range).

Our plasmon ruler-based method enables access to the complex local and global conformation dynamics of individual proteins at the level of a single protein. Therefore we extend the current paradigm “structure - function” and supplement it with a new description of “structure - time scale - function”. The ability to access the dynamics of a single protein of more than six orders of magnitude further allows me to solve important problems such as conformational heterogeneity between proteins, ergodic behaviour, and non-markovian dynamics^[6].

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Hot Electron Mediated Plasmonic Catalysis monitored by Surface-Enhanced Raman Spectroscopy employing Ag Nanorods Array

[Shashank K. Gahlaut](#), [Ilko Blad](#)

Institute of Chemistry, University of Potsdam-Golm, Germany 14476

Plasmonic materials have found their promising applications in most of the research domains in natural sciences and engineering. The metallic nanoparticles interact with the electromagnetic radiation through the collective electronic oscillations. Under some specific conditions, these oscillations resonate and generate very high intensity electromagnetic modes called surface plasmon resonance. After a series of events, these plasmons decay and the energy is transferred to the surrounding in the form of heat or highly energetic electrons. This energy is enough to induce various chemical reactions. The non-radiative decay leads to the generation of hot electrons in the metallic nanoparticles. These hot electrons are cable to induce a chemical reaction on the surface. We study the plasmonically induced chemical reactions like dimerization of molecules e.g., 4-Nitrothiophenol (4-NTP) and 4-Aminothiophenol (4-ATP) along with the dehalogenation of radiosensitizers e.g., Bromo-Adenine and Bromo-Guanine. SERS has been employed for in-situ monitoring the chemical reactions on the hot-spots on fabricated Au/Ag substrates. Dehalogenation of 8-Bromoadenine is shown here on glancing angle deposited uniform AgNRs array substrate.

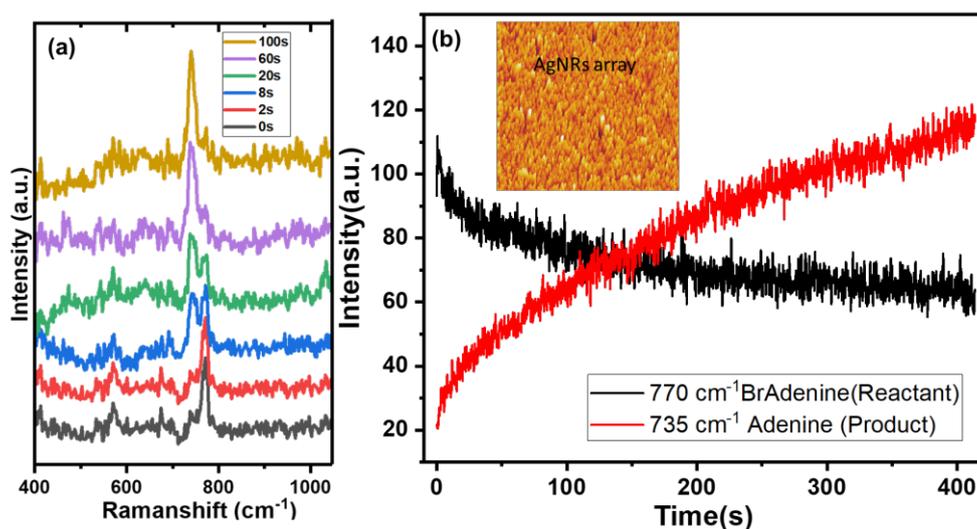


Fig. 1: (a) Time dependent SERS of 8-BromoAdenine.(b) SERS intensity kinetics of reactant (8-BrAde) and product (Ade), inset shows the AFM image of plasmonic substrate AgNRs array.

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Photonic and plasmonic resonators with topological properties for sensitive sensing and quantum applications

[Manuel R. Gonçalves](#)

Ulm University – Inst. of Experimental Physics, Albert-Einstein-Allee 11, 89081 Ulm, Germany

Fabry-Perot resonators are ubiquitous in laser systems, sensors and modern quantum applications. The optical cavity provides the field enhancement and photon lifetime required to achieve effective light-matter interaction, not possible in free space. Despite the very large Q-factor than can be achieved, one drawback of the Fabry-Perot cavities is the relatively large mode volume. On the other hand, plasmonic nanocavities, despite their weak Q-factor have very small mode volume, due to the strong light confinement and may achieve the quantum strong coupling regime.

A compromise approach to increase the Purcell factor is to use Fabry-Perot cavities of short length ($\sim \lambda/2$), or combine a Bragg mirrors with a plasmonic layer. Under certain design conditions these cavities achieve topological properties expressed by their Zak phase. The number the optical modes supported increases, in comparison to the number of classical Fabry-Perot modes. Some of them become strongly localized in the stack, whereas the others are distributed.

I will present an overview including the design method of such resonators and their optical properties, establishing the distinction with the classical Fabry-Perot modes and provide some examples of interaction with matter in external cavities, fundamental in optical sensing, but also in all quantum systems requiring very large finesse.

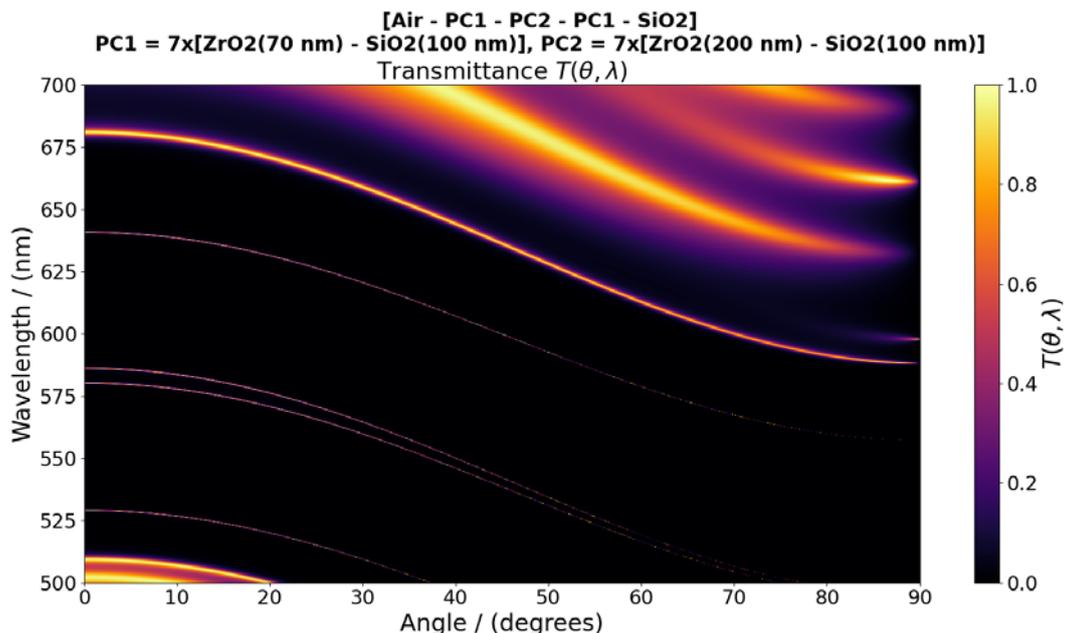


Figure 1: Transmittance modes in the bandgap of a photonic cavity using Bragg mirrors of alternating Zak phase.

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Aptamer-functionalized gold nanoparticles for the highly-sensitive dual-detection of C-reactive protein

[Alexandru-Milentie Hada](#)^{1,2}, Sorina Suarasan¹, Vlad Moldovan^{1,2}, Timea Nagy-Simon¹, Simion Astilean^{1,2}, Monica Potara¹

¹Nanobiophotonics and Laser Microspectroscopy Center, Interdisciplinary Research Institute in Bio-Nano-Sciences, Babes-Bolyai University, 400271 Cluj-Napoca, Romania

²Faculty of Physics, Babes-Bolyai University, 400084 Cluj-Napoca, Romania

C-reactive protein (CRP) is a pentameric protein produced by the liver, whose levels increase in response to infection or inflammation in the body. Additionally, chronically low levels of CRP can be an indicator for the development of future cardiovascular diseases [1]. However, the detection of CRP, nowadays, involves multiple processes that are time consuming, while requiring trained personnel to perform them. Therefore, herein, we managed to develop a dual method: colorimetric and thermoplasmonic for the easy, fast and cheap detection of CRP using aptamer-modified citrate-stabilized gold nanoparticles (apt-GNPs).

Initially, the CRP specific aptamer empowers GNPs with high stability against sodium chloride (NaCl). However, after interaction with CRP, the aptamer detaches from GNP and strongly binds to CRP, leaving the NPs exposed to NaCl from the reaction medium. This interaction with NaCl leads the unprotected GNPs to aggregation and implicitly a change in color of their colloidal solution which can be depicted even by the naked eye. The agglomeration of GNPs is proportional to the amount of CRP and therefore, by monitoring their UV-Vis spectra, the concentration of CRP can be easily determined.

Furthermore, agglomerated GNPs exhibit improved photothermal properties compared to individual ones. The interaction with more CRP will lead to a higher degree of GNP agglomeration resulting into a better light-to-heat generation. Therefore, by monitoring the temperature of the laser-irradiated colloidal solution using an IR thermal camera, the concentration of CRP was detected. In conclusion, the proposed apt-GNPs can be an excellent candidate as a point-on-care sensor for the selective and highly-sensitive dual detection of CRP.

Acknowledgement

This work was supported by a grant of the Ministry of Research, Innovation and Digitization, CNCS/CCCDI – UEFISCDI, project number PN-III-P4-ID-PCE-2020-1592, within PNCDI III.

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Rotavirus-proteins affinity dynamics via surface plasmon resonance biosensor

Anyi X. Rodriguez-Rodriguez¹, J. Augusto Galvis², César A. Herreño-Fierro³

¹Universidad Central, Carrera 5 No. 21-38, 110311 Bogotá, Colombia

²Universidad del Rosario, Calle 12C No. 6-25, 111711 Bogotá, Colombia

³Universidad Distrital Francisco José de Caldas, Carrera 3 No. 26A-40, 110311 Bogotá, Colombia

Rotavirus infection is the second most prevalent infectious disease on the planet, causing between 50 and 70 percent of acute diarrhea in children and even death [1,2]. Creating an intestinal barrier with probiotic bacteria such as *Bifidobacterium Adolescentis* is one of the effective methods for controlling the virus infection. Proteins are coated with polyethylene glycol (PEG), a polymer with a high molecular weight, to increase their resistance to stomach acid. This coating modifies the dynamics of rotavirus-protein binding, which must be comprehended. In this regard, optical techniques, such as surface plasmon resonance SPR biosensing [3], are utilized for detection.

In this work, we present the design and tuning of an SPR biosensor, as well as the characterization of the PEGylation-induced changes in virus-protein affinity and binding dynamics.

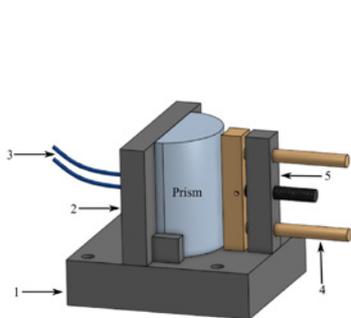


Fig. 1

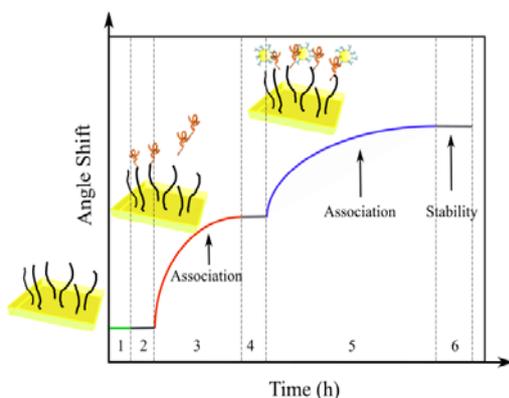


Fig. 2

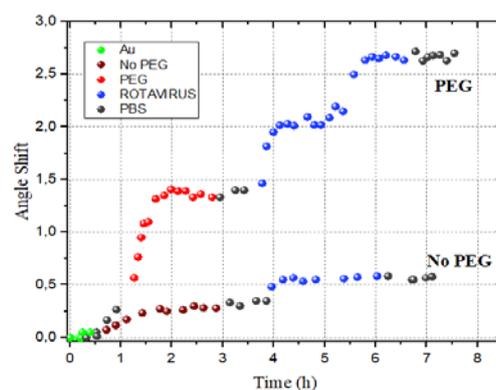


Fig. 3

Fig. 1: Scheme of the home-made holder for the optical transducer

Fig. 2: Schematics of an affinity sensorgram for Proteins and Rotavirus with thiolated molecules

Fig. 3: Affinity sensorgram for PEGylated and non-PEGylated Proteins (25%) with Rotavirus (50%)

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Plasmonic Surface Lattice Resonances in Arrays of Gold Nanoparticles

Carlos J. Rojas-Bejarano¹, Mario Zapata-Herrera^{2,3}, César A. Herreño-Fierro³

¹Universidad Central, Carrera 5 No. 21-38, 110311 Bogotá, Colombia

²Materials Physics Center CSIC-UPV/EHU, Paseo Manuel de Lardizabal 5 20018, Donostia-San Sebastián, Spain

³Universidad Distrital Francisco José de Caldas, Carrera 3 No. 26A-40, 110311 Bogotá, Colombia

In this work, we performed a systematic study on the optical response of periodic arrays of gold nanoparticles (AuNPs). Specifically, we analyze the influence of the geometrical features of the nanoparticles (shape and size), the dielectric environment (refractive index), and the lattice parameter (in square lattices), on the quality factor (Q) of the localized surface plasmon resonances (LSPRs) for a variety of configurations. We calculate the transmittance (T) in different systems through the variation of geometrical parameters using the Finite Element Method (FEM), implemented in the commercial software COMSOL Multiphysics®. Our results allow us to characterize the sensitivity of these surface lattice resonances (SLRs) to changes in the dielectric environment as a principle of operation in conceptual prototypes of plasmonic transducers for bio-detection. The influence of the geometrical parameters on the excitation of surface plasmons in periodically distributed nanoparticles serves as a theoretical basis for the improvement of the control of the optical response of these systems and opens the way for the analysis of more complex realistic geometries and their applications in biosensors.

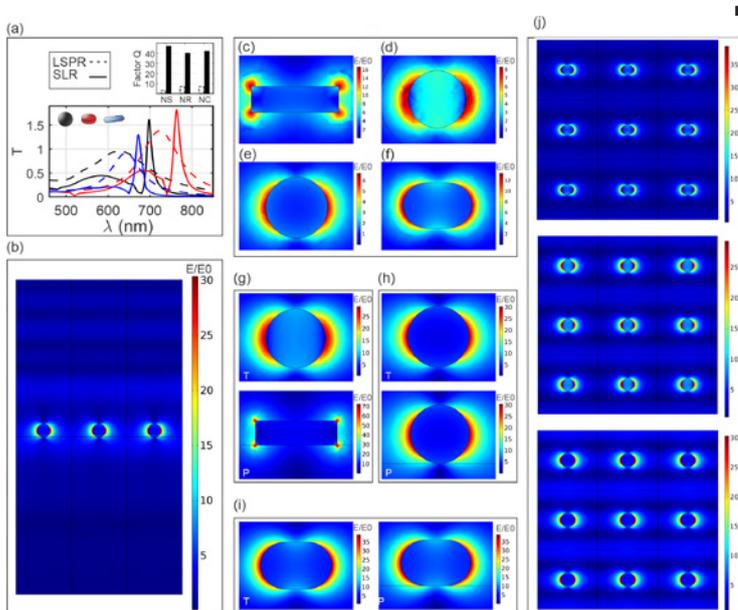


Fig. 1

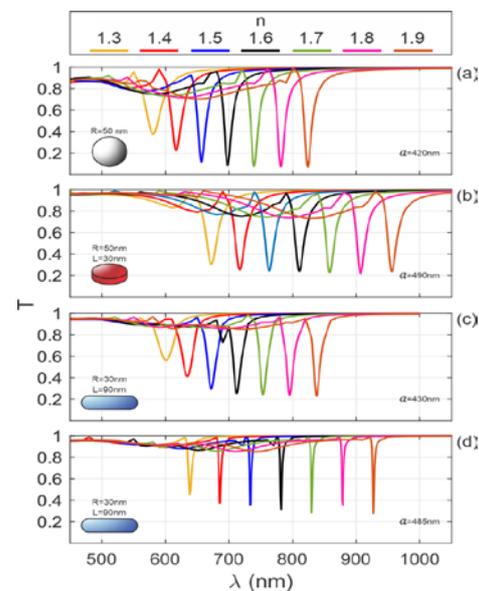


Fig. 2

Fig. 1: (a) Transmittance spectra of square arrays (solid lines) and isolated (dashed lines) of AuNPs. Gold Nanospheres ($R=50$ nm; black), nanocylinders ($R = 50$ nm, $H = 30$ nm; blue) and nanorods ($R = 30$ nm, $L = 30$ nm; red) were studied. A medium with a refractive index (RI) of 1.6 for the nanosphere arrays and 1.5 for the remaining studied systems, as well as incident light normal to the lattice plane, is considered. The light source is linearly polarized along the plane of the nanodisks and the axis of the nanorods, respectively. Color maps represent electric field amplitudes E/E_0 at resonance, calculated at certain planes. For isolated NPs (c) and (d) correspond, respectively, to the transverse and parallel planes for the nanocylinder, while (e) and (f) correspond to the transverse planes for the nanosphere and nanorod, respectively. For NPs arrays, (g), (h) and (i) show the response of single a nanodisk, nanosphere and nanoroad, respectively, meanwhile (b) correspond to a transversal plane of nanospheres, and (j) to parallel planes to the arrays of each geometry.

Fig. 2: Transmittance spectra for periodic arrays of (a) nanospheres ($R = 50$ nm) with lattice constant 420 nm, (b) nanocylinders ($R = 50$ nm, $L = 30$ nm) with lattice constant 490 nm, and nanorods ($R = 30$ nm, $L = 90$ nm) with lattice constants (c) 430 and (d) 485 nm. All systems are immersed in a symmetric optical medium of varying refractive index n . The incident light is linearly polarized in the x-direction.

Near Infrared Plasmonic & reduced Graphene Oxide Hybrid Nanoplatfom for Photothermal Therapy

Alexandru Holca^{1,2}, Vlad Cucuiet¹, Klara Magyari³, Simion Aştilean^{2,4}, Monica Focşan²

1 Faculty of Physics, Babes-Bolyai University, 1 M. Kogalniceanu Str., 400084 Cluj-Napoca, Romania

2 Nanobiophotonics and Laser Microspectroscopy Center, Interdisciplinary Research Institute in Bio-Nano-Sciences, Babes-Bolyai University, 42 T. Laurian Str., 400271 Cluj-Napoca, Romania

3 Nanostructured Materials and Bio-Nano-Interfaces Center, Interdisciplinary Research Institute on Bio-Nano-Sciences, Babeş-Bolyai University, 42 T. Laurian Str., 400271 Cluj-Napoca, Romania

4 Biomolecular Physics Department, Faculty of Physics, Babes-Bolyai University, 1 M. Kogalniceanu Str., 400084 Cluj-Napoca, Romania

Photothermal therapy is a non-invasive treatment for cancer therapy that provides excellent results due to the increase of the temperature in the cancer cells [1]. Recently, novel hybrid nanomaterials based on graphene and plasmonic nanoparticles have gained high consideration as photothermal agents on the strength of the tunability of the plasmonic nanoparticles absorption maximum in the near infrared (NIR) region (700 nm-1350 nm). Compared to the visible light range, near infrared range, also called biological window, presents better penetration depth and transparency for biological tissues [2].

As an emerging necessity to develop new cancer treatment, this study provides new perspectives on the photothermal therapy by designing a unique hybrid nanotherapeutic platform based on plasmonic nanoparticles and polymer-reduced graphene oxide (rGO). Concretely, the highly photo-responsive gold nanorods nanoparticles (GNRs) and polyethylene imine reduced graphene oxide (PEI-rGO) were synergistically combined to operate as effective intrinsic photothermal agents by generating heat under NIR light excitation. While GNRs with controlled plasmonic response at 777 nm were synthesized using the seed mediated procedure, GO was firstly obtained by a modified Hummers method and then efficiently reduced using the biocompatible PEI polymer. To note that PEI was used herein not only as reducing and stabilizing agent for the graphene oxide (GO) but also to act as an excellent shell to bind the prior synthesized GNRs. The successful generation of the as-formed hybrid nanoplatfom was rigorously investigated by Raman, Fourier-transform infrared spectroscopy as well as by Transmission Electron Microscopy investigations. Next, the photothermal effect of the final hybrid nanoplatfom (rGO-PEI@GNRs) was evaluated using a 785 nm laser. To further demonstrate the biocompatibility of rGO-PEI@GNRs, MTT assay was used. Conclusive results show low dark cytotoxicity of the nanoplatfom proving the potential *in vitro* and *in vivo* application of our designed photothermal agents.

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Monitoring Photolipid Bilayer Membrane Switching with Plasmonic Nanorods

[Dominik Kammerer](#), Jinhua Zhang, Francis Schuknecht, Ludwig Habermann, Alexander Pattis, Stefanie D. Pritzl, Theobald Lohmüller

Chair for Photonics and Optoelectronics, Nano-Institute Munich, Department of Physics, Ludwig-Maximilians-Universität, Königinstraße 10, 80539 Munich, Germany.

Photoswitchable lipids (named photolipids) are highly effective tools to control the physical properties of lipid bilayer membranes with light. [1-4] However, analyzing the switching dynamics in a single bilayer locally and *in situ* is challenging due to a lack of sensitive tools for monitoring the very small changes in lipid conformation and membrane thickness (< 1 nm). Here, we demonstrate a new approach to analyze the photoisomerization of photolipid membranes on the nanoscale via plasmonic sensing.

We devised an experiment, where gold nanorods are deposited on a glass substrate and coated with a supported photolipid bilayer (SPB). The photosensitive azobenzene group in the lipid tails is switched between a *trans* and *cis* form with UV (365 nm) and blue light (465 nm), while the dark-field scattering spectra of individual nanorods are simultaneously measured. We find that lipid photoisomerization leads to a shift of the nanorod's plasmon resonance that is reversible over many switching cycles. Furthermore, we show that the corresponding photoisomerization dynamics of SPBs can be analyzed with high accuracy by time-dependent measurements of the plasmon resonance shift.

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Investigating ligand binding to G-quadruplex DNA at the single-molecule level via plasmon-enhanced fluorescence

Ashish Kar^{1,2*}, Saumyakanti Khatua¹ & Bhaskar Datta^{1*}

¹ Chemistry Discipline, Indian Institute of Technology Gandhinagar, Palaj, Gujarat-382355, India

² Present address : Molecular Imaging and Photonics Unit, Department of Chemistry, KU Leuven, Celestijnenlaan 200F, Leuven, Belgium,

Guanine-rich sequences tend to fold into secondary structures called G-quadruplexes (GQ). The human telomeres consist of a 3' single-stranded TTAGGG repeat overhang which can form GQs. Telomeres in cancerous cells, unlike normal cells, do not shorten on replication due to over-expression of the telomerase enzyme, causing their indefinite growth. GQs can inhibit the activity of telomerase thereby projecting a straight-forward target for anticancer therapeutics. [1] This has made GQs an interesting target site for potential anticancer therapy and has triggered a large number of biophysical studies focusing on GQs structure and interaction dynamics. Single-molecule measurements are key to understanding the binding behaviour of GQ-targeting ligands which in turn is critical for the deployment of such ligands in a medical or technological paradigm. [2,3]

In this work, we present a new approach of using plasmon-enhanced fluorescence as a readout to study the interaction of a GQ stabilizing ligand 5,10,15,20-tetrakis(N-methyl-4-pyridyl)porphyrin, TmPyP4 with human telomeric (hTelo) DNA GQ sequences at the single-molecule level. In our study, single gold nanorods were functionalized in situ with hTelo GQ DNA, and the plasmonic enhancement of fluorescence in the vicinity of gold nanorods was used to investigate TmPyP4 binding to the GQs in real-time. The time trajectories revealed a clear distinction between TmPyP4 binding interactions with parallel and antiparallel topologies of hTelo sequences. Further, this method enabled real-time visualization of the ligands' dynamic binding/unbinding with GQs. We believe the use of enhanced fluorescence as the readout will trigger future studies of GQ binding ligands at the single molecule level, particularly those of weakly emitting nature, which was elusive.

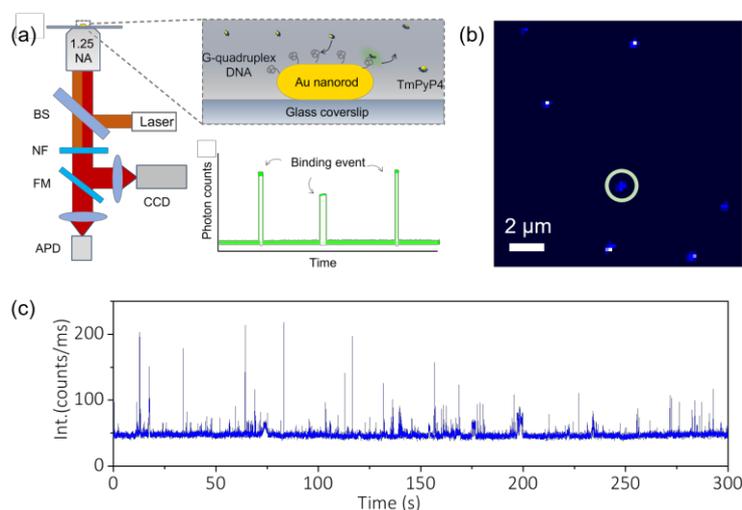


Figure 1: (a) Schematic illustration of the experimental setup, (b) One-photon luminescence image of single gold nanorods on glass substrate, (c) Time trace taken on a single DNA modified-nanorod in presence of TmPyP₄.

Reference:

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Plasmon-enhanced diffractive supercells

Hamid Keshmiri¹, Fahimeh Armin², Frank Schreiber¹

¹Federal Institute for Materials Research and Testing, 12205 Berlin, Germany

²Department of Computer Science, Université du Québec à Montréal, H2X 3Y7 Montréal, Canada

Multiple diffractive surface modulations can concurrently couple the light to several electromagnetic surface waves [1]. We present a multi-resonant plasmonic supercell structure with a broad range of applicability in harvesting the light over an extensive wavelength range and angles of incidence [2-3]. The resonance bands were realized by incorporation of several encoded periods in a conventional diffraction grating structure, ensuring that the properties of a single periodic structure in excitation wavelengths and angular dependency were preserved by the supported supercell structure. In Fig. 1, the design concept for three encoded periods corresponding to different spatial frequencies of surface modulation function at Ag:Ge interface shows a plasmon-mediated absorption probability of 18.13% in a wide wavelength band of 400-1200 nm. This translates to an enhanced absorption factor of 7.5% in the Ge active layer for a multi-band structure compared to that of a single band.

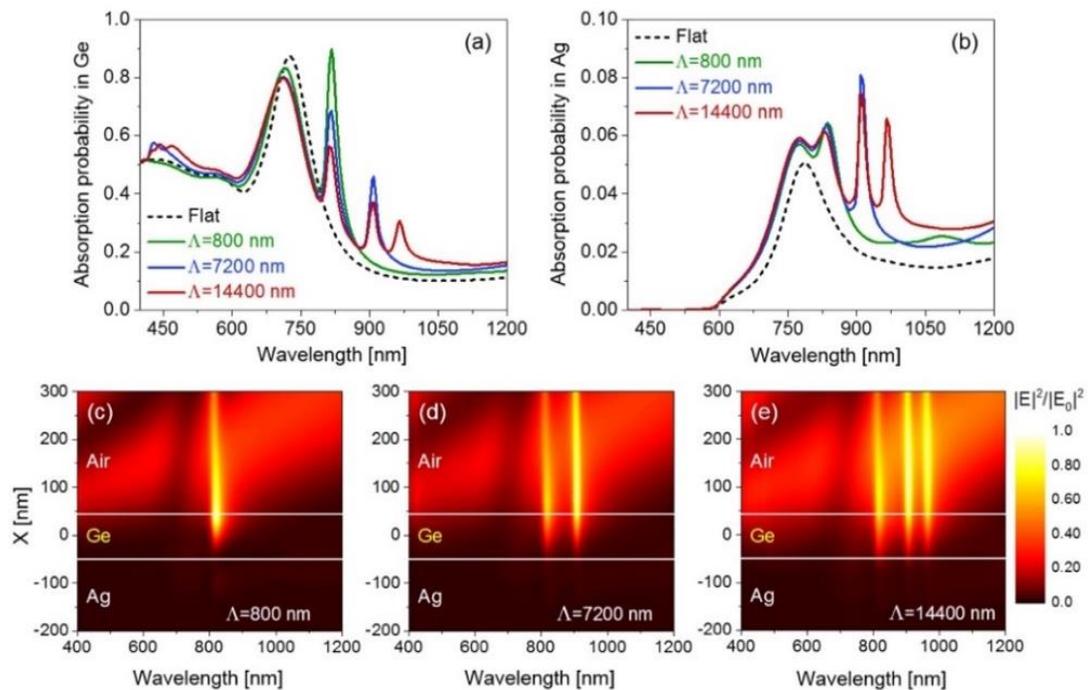


Fig. 1: Absorption probability in (a) Ag, and (b) Ge layers for different periods. The dash lines show the absorption of flat structures. (c) Normalized electric field intensity corresponding to gratings with $\Lambda=800$ nm, (d) $\Lambda=7200$ nm, and (e) $\Lambda=14400$ nm within their layer configuration.

This work is based on realistic theoretical and experimental data to show the modal interferences in multi-diffractive grating structures [2-3], and how a plasmon-mediated absorption band extends over a wide wavelength window upon the surface development. The utilization of these nanoarchitectures in lab-on-chip biosystems will also be discussed.

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Gold Nanorod DNA Origami Antennas for 3 Orders of Magnitude Fluorescence Enhancement in NIR

[Karol Kołataj](#)^{§, †}, [Kateryna Trofymchuk](#)[†], [Viktorija Glembockyte](#)[†], [Fangjia Zhu](#)[§], [Guillermo A. Acuna](#)[§], [Tim Liedl](#)[‡], [Philip Tinnefeld](#)^{†*}

[§] Département de Physique - Photonic Nanosystems, Université de Fribourg - Faculté des Sciences et Médecine, Chemin de Musée 3, CH-1700 Fribourg, Switzerland, karol.kolataj@unifr.ch

[†] Department of Chemistry and Center for NanoScience, Ludwig-Maximilians-Universität München, 81377 München, Germany

[‡] Faculty of Physics and Center for NanoScience (CeNS), Ludwig-Maximilians-University, Geschwister-Scholl-Platz 1, 80539 Munich, Germany

For the last few years, plasmonic sensors based on gold and silver nanoparticles have been widely used in various spectral techniques.[1] Main features of plasmonic nanoparticles that render them remarkably attractive sensing materials are their optical properties, namely a significant enhancement of the electromagnetic field near the surface of irradiated nanoparticle. Importantly, the electric field is not evenly distributed around the nanoparticles. The strongest electromagnetic field enhancement occurs at the sharp edges of nanoparticles or in the gaps between them. [2,3] Therefore, for high signal amplification, it is crucial to find a reliable and high-precision method for fabricating plasmonic nanosensors. Because of the addressability, specificity, and nanometer precision, DNA origami becomes a natural candidate for synthesizing versatile antenna structures, especially when employing anisotropic nanoparticles. Nevertheless, still high majority of DNA origami-based sensors used in fluorescence utilize spherical gold or silver nanoparticles. [4]

Here we present the synthesis of DNA origami dimer antenna based on Au nanorods enabling fluorescence enhancement of a conventional NIR dyes up to 1600 folds, that is, to the best of our knowledge, the highest values reached in a self-assembled NA with an ordinary QY dye precisely positioned in the hotspot (Figure 1). [5] This was possible to achieve by using NRs of relatively big size (~67x20 nm) which created a higher electric field in the plasmonic hotspot, and choosing dyes with matching spectral overlap with the plasmonic near-field. Advantage of using NRs with an anisotropic shape over anisotropic NPs for fluorescence enhancement applications was demonstrated by the direct comparison of dimer AuNRs antenna with DNA origami nanantenna containing dimer of spherical NPs of the similar volume (40 nm in diameter).

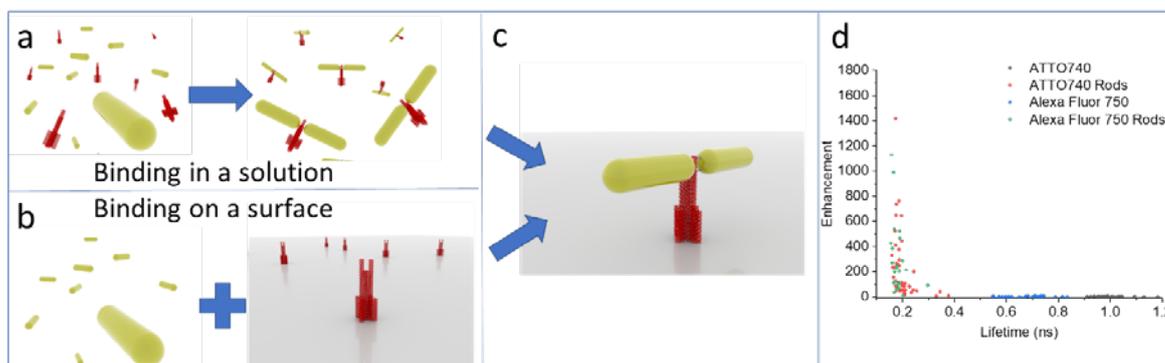


Figure 1. Schematic representation of the synthesis of AuNRs antennas for fluorescence measurements (c) by (a) solution and (b) surface binding method. (d) Fluorescence enhancement distribution of ATTO 740 and Alexa Fluor 750 with AuNRs antennas.

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NanoSPR for Biological Sensing

[Alena Kuzmina](#)¹, [Sirin Celiksoy](#)¹, [Karl Wandner](#)¹, [Thorsten Hugel](#)² and [Carsten Sönnichsen](#)¹

¹Department of Chemistry, University of Mainz, Duesbergweg 10-14, 55128 Mainz, Germany

²Institute of Physical Chemistry, University of Freiburg, Albertstraße 23a, D-79104 Freiburg, Germany

Due to their photostability, small size, and large light scattering cross-section, gold nanorods find application as sensors for the attachment of macro- and bio-molecules (Nano-SPR). These nanosensors can be adjusted to address specific biological problems by varying the particles' dimensions, geometry and their surface functionalization. An advantage over fluorescence based methods is the unlimited photo-stability.^[1,2]

In particular, I present how NanoSPR can provide answers to questions of both qualitative and quantitative nature by showing specific applications such as determination of protein binding affinities^[4], visualization of the oscillation of a dynamic non-equilibrium protein system (MinD-MinE) and detection of single protein dynamics of Hsp90^[6].

These examples of NanoSPR demonstrate how successful applications rely on the selection of a case-appropriate signal read-out method, optimizing the bio-chemical nature of the nanosensor as well as balancing the respective advantages and disadvantages of each method.^[3]

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Plasmonic bound states in the continuum for strong light-matter interaction.

Yao Liang, Jingcheng Zhang, Din Ping Tsai*

Department of Electrical Engineering, City University of Hong Kong, Kowloon, 999077, Hong Kong.

The concept of optical bound states in the continuum (BICs) offers an important physical mechanism for engineering high-quality (high-Q) resonances. However, current studies of BICs have been mainly limited to lossless dielectric nanoparticles and structured dielectric metasurfaces. Here, employing the BICs physics, we present results on the realization of high Q-factor plasmonic resonances in lossy metallic nanostructures. Also, we reveal their engaging new properties, such as giant field enhancement, flat-band effects for lattice resonances, and coexistence of giant circular dichroism and high Q-factor resonance. Specifically, our investigation includes 3 aspects:

1. It was generally believed that the giant near-field enhancement in plasmonic resonances is solely determined by ultra-small mode volume. We challenge this limitation and argue that the Q-factor does have an important impact on light field enhancement. We show a field enhancement factor of more than 10,000 times for plasmonic quasi-BICs at critical coupling conditions (perfect absorption).
2. Plasmonic surface lattice resonances (SLRs) are known for their high Q-factor resonances. However, SLRs can often be excited by collimated light but face fundamental challenges for focused light excitation. This is because of the strong angular dispersion effects in SLRs. We show that by using butterfly wings plasmonic nanostructures, a flat-band can be created to solve this problem.
3. Current research on chiral BICs faces a fundamental trade-off between the circular dichroism and Q-factor for chiral quasi-BIC resonances. Here, employing plasmonic integrated resonance units, we address this challenge and achieve high Q-factor chiral plasmonic BICs with strong circular dichroism.

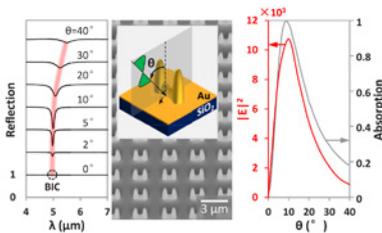


Fig. 1

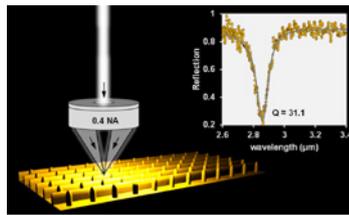


Fig. 2

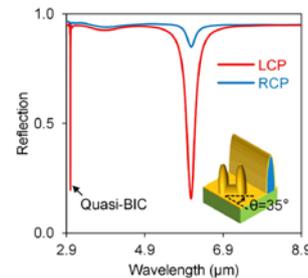


Fig. 3

Fig. 1: Plasmonic BICs for giant field enhancement.^[1]

Fig. 2: Plasmonic lattice resonance excited by focused light with weak spatial coherence.^[2]

Fig. 3: Chiral plasmonic quasi-BICs with giant circular dichroism.^[3]

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Raman-based Detection of Antibiotics and Metabolites in Pharmaceutical Formulations and Clinical-relevant Matrices

[Chen Liu](#), Jürgen Popp, Dana Cialla-May

Leibniz Institute of Photonic Technology, Member of Leibniz Health Technologies, Member of the Leibniz Centre for Photonics in Infection Research (LPI), Albert-Einstein-Straße 9, 07745 Jena, Germany. Institute of Physical Chemistry (IPC) and Abbe Center of Photonics (ACP), Friedrich Schiller University Jena, Member of the Leibniz Centre for Photonics in Infection Research (LPI), Helmholtzweg 4, 07743 Jena, Germany

Raman spectroscopy is a powerful tool for bioanalytical detection methods due to its molecular-specific fingerprint information. The limitation associated with the small Raman cross section can be overcome by the application of powerful plasmonic-active nanostructured sensing surfaces, i.e. by means of surface-enhanced Raman spectroscopy (SERS). Thus, analyte molecules in the μM range or lower can be detected with high specificity.

A Raman-based label-free analytical method was developed to detect the antibiotic ciprofloxacin (CIP) in various pharmaceutical formulations. [1] The Raman spectral analysis is performed for semi-quantification in the case of a low background Raman signal, i.e., the signal originating from the excipient and carrier substance of the formulation does not interfere with the fingerprint spectrum of CIP. In the case of a background spectrum rich in Raman modes originating from the excipient and carrier substance of the formulation, the pharmaceutical formulation is diluted 1:5000, and thus, the background signal is undetectable. Due to the high affinity of CIP towards metallic surfaces, SERS is applied to allow for the sensitive detection of this antibiotic even in complex pharmaceutical formulations with high dilution ratios. The developed measurement routine can be applied to monitor the degradation of the active component ciprofloxacin within the pharmaceutical formulation.

Moreover, pyrazinoic acid (POA) is detected in cultural supernatants by using specially designed gold nanoparticles coated with Prussian blue. POA is the metabolite of the drug pyrazinamide (PZA), applied in tuberculosis treatment. [2] Here, POA complexes due to the presence of Fe(II) in Prussian blue and can be detected quantitatively by means of SERS applying Prussian blue coated SERS probes in a complex biological matrix. This illustrates the potential of the proposed detection scheme for an assessment of the resistance of *M. tuberculosis* in cultures as only sensitive strains allow the metabolism from PZA to POA.

Finally, we developed a SERS-based detection scheme using silicon nanowires decorated with silver nanoparticles, fabricated by means of metal-assisted chemical etching combined with chemical deposition, to detect the antibiotic ceftriaxone (CRO) in spiked blood plasma and microdialysis solutions. We successfully detected CRO in both matrices with an LOD of 0.101 mM in blood plasma and 1.5 μM in microdialysate.

Acknowledgement: We gratefully acknowledge the Federal Ministry of Education and Research, Germany (BMBF) funding the grant InfectoGnostics (13GW0096F).

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Characterization of the sensing potential of assembled plasmonic nanostructures

[Yeshni Luximun](#), [Pia Pritzke](#), [Amarildo Hoxha](#), [Laura Maria Palacios-Narvaez](#),
[Mario Zapata-Herrera](#), [Andrea Csáki](#), [Wolfgang Fritzsche](#)

[Leibniz Institute of Photonic Technology, Albert-Einstein-Straße 9, 07745 Jena, Germany](#)

The use of plasmonic nanostructures in the field of label-free biosensing has generated an extensive research interest in the past decades. Their unique optical property of enhancing the absorption- and scattering-effect of light by their localised surface plasmon resonance (LSPR) [1] makes them a viable tool for nano-scale sensing.

This work aims to produce highly sensitive plasmonic biosensors with a high-throughput and low-cost fabrication technique by making use of nanoimprint lithography (NIL) to create assembled nanostructures. These nanostructures have the potential to exhibit plasmon coupling and Fano resonances [2] which results in highly sensitive sensors.

To enable a high degree of control over the arrangement and position of the nanoparticles, a nanohole-array in poly(methyl methacrylate) (PMMA) was fabricated by Electron Beam Lithography (EBL) as a model template (Fig. 1). The dimension and shape of the nanoholes were varied to realise different nanoparticle structures, in order to optimise the template-dimension for NIL. This template was chemically functionalized, which allows the selective immobilization of gold nanoparticles in the nanoholes. For the ultramicroscopic characterization of the nanostructures, methods like the dark-field and atomic force microscopy (AFM) imaging were used (Fig. 2). The spectral information was obtained by a micro-spectroscopic setup and compared to the pyGDM simulations.

A reliable method for the binding of the nanoparticles on the substrate was implemented and a reproducible procedure for the fabrication of a plasmonic microarray was successfully established. The dimension and shape of the microarray were the key factors which were optimised for the realisation of different structures. The spectra measurements highly correspond to the simulations. In addition, the sensitivity of the nanostructures for bioanalytical application will be determined. The implementation of shape-anisotropic nanoparticle, due to their superior sensitivity is planned for the future.

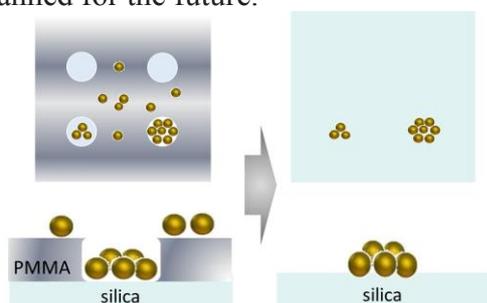


Fig. 1

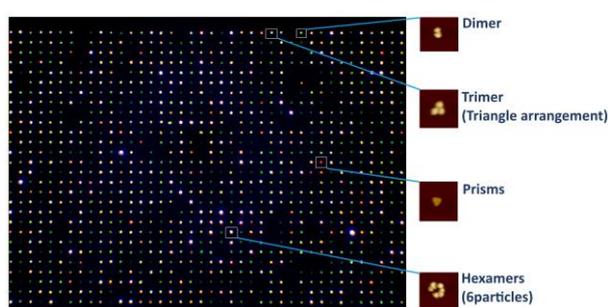


Fig. 2

Fig. 1: Dark-field images prior to and after PMMA lift-off

Fig. 2: Dark-field and AFM images of the immobilized Nanoparticles for LSPR measurements

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Development of EVs Detection Device Based on AC Electroosmosis

Ibuki Machi, Masanori Eguchi, Shinichi Tanaka, Mami Okada, Naoto Kajitani

National Institute of Technology (KOSEN), Kure College, 2-2-11, Agaminami, Kure, 737-8506 Hiroshima, Japan

The number of patients with psychiatric disorders such as depression and dementia has been increasing rapidly in Japan. Currently, the diagnosis of psychiatric disorders is primarily made based on multiple careful interviews by physicians and diagnostic imaging such as MRI. This approach has not been established with clear criteria to determine psychiatric disease names, so the development of an objective diagnostic method using biomarkers is desired for both physicians and patients. EVs (Extracellular Vesicles) are one of the particles secreted by cells and contain proteins, miRNAs, mRNAs, etc. They are expected to be biomarkers for various diseases because they reflect the cells which secreted them. Recently, EVs derived from cerebrospinal fluid in blood were reported to be useful as a biomarker for Alzheimer's disease¹. This enables liquid biopsy, which requires only bodily fluid sampling to perform the test, thus this will provide merits for patients with minimal invasion and quick testing. However, EVs are tiny, and those from brain cells are only very small quantities exist in the peripheral blood. Therefore, highly sensitive techniques are required to isolate and detect them.

In this paper, we developed the collection device (Fig.1) for rapid collection of EVs from blood by combining dielectrophoresis (A phenomenon in which a force is exerted on a dielectric particle when it is subjected to a non-uniform electric field) and AC electroosmosis (A phenomenon in which the AC electric field and the interfacial ions between the electrode and the aqueous solution cause a flow of solution toward the center of the electrode). The device consists of an ITO electrode (transparent electrode) deposited on a glass substrate and an insulating film placed on the ITO electrode. We observed the behaviors of EVs and HEK293 cells (Human Embryonic Kidney cells) under a non-uniform electric field with this device. The applied voltage and frequency were 10 V_{pp} and 30 kHz, respectively. As a result, EVs were collected on the circular electrode by AC electroosmosis. On the other hand, HEK293 cells were moved away from the electrode by negative DEP.

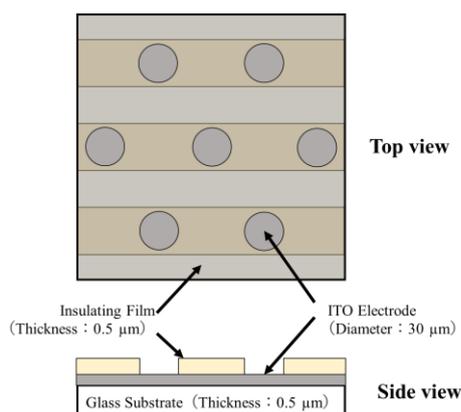


Fig. 1

Fig. 1: Device Structure

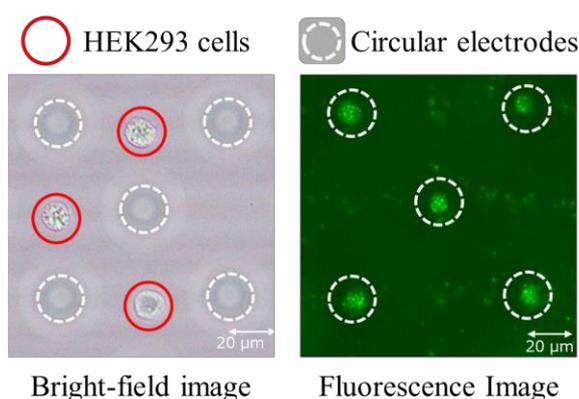


Fig. 2

Fig. 2: Isolated EVs and HEK293 cells

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Large $Ti_3C_2T_x$ MXene dimers as SERS substrates

[Hayk Minassian](#), [Armen Melikyan](#), [Petros Petrosyan](#), [Manuel Gonçalves](#)

[A.Alikhanian National Science Laboratory, Alikhanyan Str. Build. 2, 0036, Yerevan, Armenia](#)

SERS process from R6G molecule near the large $Ti_3C_2T_x$ MXene dimer of linear sizes $1 \mu k \div 2 \mu k$ is analyzed theoretically. The flakes in the dimer are modeled as nanoparticles with lateral shapes similar to synthesized samples. For numerical calculations the dye molecule is modeled as a small sphere with wavelength dependent polarizability coinciding with experimentally determined one. The SERS enhancement factor (EF) dependence on wavelength in case of dimer of nanoellipsoids (NE) with maximal value $1.4 \cdot 10^7$ close to experiment [1] is presented in the Fig.1.

It is demonstrated that the enhancement of SERS is conditioned by increasing lightning rod and hot spot effects due to overlapping of interband transitions (IBT), quadrupole longitudinal and transversal surface plasmon (QLSP, QTSP) resonances identified in [1], with the R6G molecular absorption resonance. The experimental data on SERS EF for the R6G molecule on a MXene substrate vary in the range of $10^5 \div 10^7$ (see e.g. [2]), which agrees well with theoretical estimations for the R6G molecule near the apex of MXene NP.

To further clarify the role of hot spot effect in SERS we calculated the absorption cross-section in the dimer nanospheroids with axes 1000 nm and 400 nm for 4 values of interparticle gap (see Fig.2.) As it can be seen in vis-NIR range the absorption cross – section and correspondingly the EF are not sensitive to interparticle gap size. Thus, due to less sensitivity of IBT and QLSP and QTSP resonances with respect to the dimer shape and gap size, easy synthesized MXene nanoparticles randomly scattered on the dielectric substrate can present practical interest for SERS applications. Interestingly, the Fano dip in absorption spectra at 1440 nm appears to be independent on gap size (see Fig.2). Obviously, this peculiarity can be important for molecular sensing based on the optical properties of plasmonic nanoparticles.

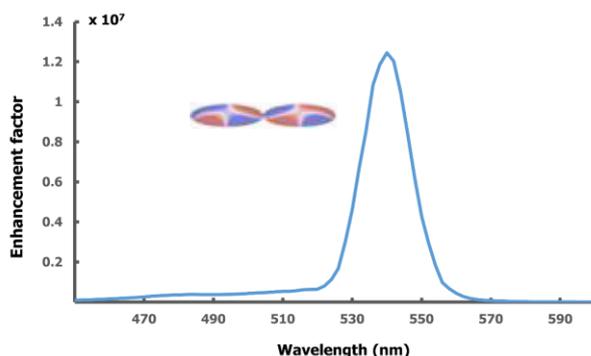


Fig. 1

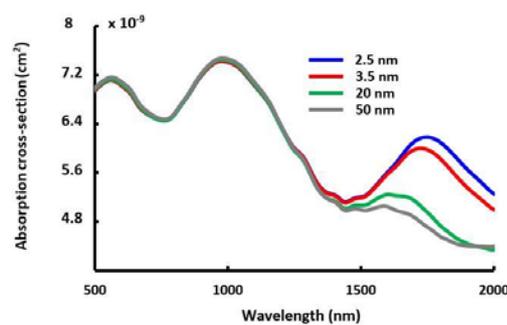


Fig. 2

Fig.1: EF for NE MXene dimer with large axis of 1000 nm . Insert-charge density distribution.

Fig.2:IBT, QLSP and QTSP resonancies and Fano dip in absorption spectra of dimer.

Acknowledgment: The work was supported by the Science Committee of RA, in the frames of the research project № 21T-1C169.

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[2] M. Gonçalves et al. *Photonics* 2021, 1, 0.

Towards modulating near-field plasmonic coupling for enhanced optical spectroscopy

Dario Cattozzo Mor¹, Simone Auer², Yevhenii Morozov², Thorben Jaik³, Fiona Diehl³, Ulrich Jonas³, Jakub Dostalek^{1,2}

¹FZU-Institute of Physics, Czech Academy of Sciences, Prague, Czech Republic,

²Austrian Institute of Technology GmbH, Tulln an der Donau, Austria,

³Macromolecular Chemistry, Department of Chemistry-Biology, University of Siegen, Siegen, Germany

Metallic nanostructures allow for tight confinement of electromagnetic field through the resonant excitation of surface plasmons. The associated enhancement of field intensity offers efficient means for the amplification of weak optical spectroscopy signals (such as fluorescence, Raman scattering, or infrared absorption). Typically, the metallic nanostructures are made static. A possible route to expand the spectrum of applications and performance of plasmon-enhanced spectroscopy tools is pursued, based on responsive hydrogel materials that act as artificial muscles and provide on-demand, reversible reconfiguration of plasmonic hotspots^[1]. Hydrogels are three-dimensional polymer networks with the ability to intake large amounts of water. Some classes of thermo-responsive hydrogels can be reversibly toggled between two states – swollen and collapsed – by modulating their temperature T .

In this work, we use poly(N-isopropylacrylamide)-based responsive terpolymers (pNIPAAm). Polystyrene (PS) nanoparticles were dispersed in the hydrogels, allowing precise control on the temperature-induced changes of the swelling ratio^[2]. Thicknesses of the composite layer in air and in water are studied via SPR and OWS.

When immersed in water, the swelling of pNIPAAm-only, surface-attached hydrogel discs leads to perturbation of their own the geometry, due to lateral stress. The incorporation of PS nanoparticles in the gel matrix allows for a mechanically more rigid structure and reduce the impact of buckling.

This controlled actuation mechanism finds various applications in plasmonic nanomaterials. Here we present the concept of a microscopic responsive hydrogel structure that allows the modulation of the distance between metallic nanoparticles and a flat metal surface, for reversible near-field coupling and formation of a gap mode. The plasmonic coupling can be exploited for probing of molecules, by plasmonically-enhanced optical spectroscopy.

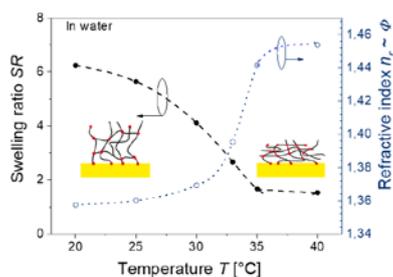


Fig. 1

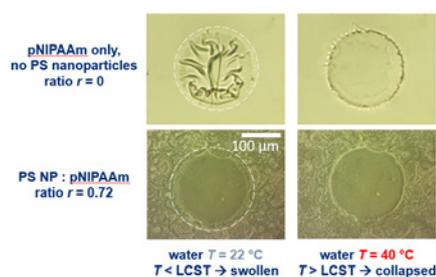


Fig. 2

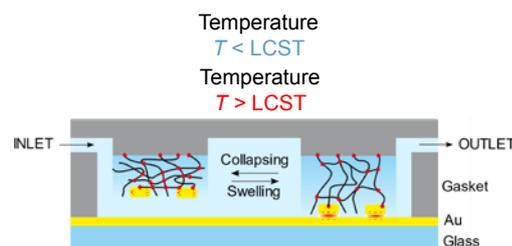


Fig. 3

Fig. 1: Swelling/collapse mechanism of the hydrogel structures, as function of temperature

Fig. 2: Swelling uniformity and rigidness for different PS NP concentration in solution

Fig. 3: Flow-cell concept, featuring reconfigurable onset of near-field coupling at nanoparticle-surface gap.

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Mathematical model to predict the cellular internalization of gold nanoparticles.

Orlando Narváez González¹, César A. Herreño-Fierro¹, Julian Mateo Zutta², Adriana De Mendoza².

¹Universidad Distrital Francisco José de Caldas, Faculty of Sciences and Education

²Pontificia Universidad Javeriana, Physics Department

Cancer is a severe health problem all around the world; taking about 10 million lives just in 2020. In the fight against cancer, new approaches have emerged, including nanoparticle therapy. Noble metal nanoparticles, especially gold, have shown to be promising for oncological theragnostic (diagnosis and therapy). Their potential comes from their surface plasmon resonance-enhanced light scattering and absorption. However, nanomedicine treatments are not yet a common clinical practice because the underlying mechanisms, and therefore safety, are not fully elucidated from preclinical studies. In this vein, mathematical models help to better understand many of the unknowns.

We propose a mathematical model to predict the number of nanoparticles (NPs) internalized in the cell, from the interactions between the nanoparticles and the cell. This compartmental model accounts for the spatiotemporal evolution of various entities, such as particles, receptors, and particle–receptor complexes. Within this model, the cellular uptake of NPs can be simple diffusion or mediated by free receptors in the cell membrane. In the latter mechanism, NPs are grouped to form an optimal radius to break the thermodynamic barrier in the cell membrane. Notwithstanding, the internalization rates depend not only on the size of clusters but also on factors such as geometry, size, and electric charge, among others. Here we explore the effect of some of them, aiming to help pave the road to safe and effective treatments with nanoparticles.

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Insulator-based Dielectrophoresis Device Utilizing Positive Dielectrophoresis for Dielectric Characteristics Measurement

Koki Nietani, Kotaro Matsumura, Ryu Nakabayashi, Masanori Eguchi

National Institute of Technology (KOSEN), Kure College, 2-2-11, Agaminami, Kure, 737-8506 Hiroshima, Japan

The technology for isolating and analyzing specific cells from many types of cells without damaging them has advanced dramatically. Above all, dielectrophoresis (DEP), utilizing the dielectric characteristics of cells, has merits of being noninvasive and no labeling is required. Dielectric characteristics are determined by the structure and electrical properties of the cell and can be evaluated using the velocity of DEP. Medical applications of DEP include separation of cancer cells from normal cells [1], separation of living cells from dead cells [2], and concentration of cancer cells [3]. Thus, the measurement of detailed dielectric characteristics of biological cells is extremely important for the medical application of DEP devices. However, dielectric characteristics of biological cells are varied: not only between abnormal cells like cancer cells and normal cells, but also among the same type cells. Therefore single-cell analysis is required for more detailed analysis. Furthermore, the measurement of dielectric characteristics uses the frequency property of cells. However, electrode-based DEP (eDEP) devices, which are commonly used as DEP devices, the electric field is concentrated at the edge of the electrode in positive DEP, causing cells adherence.

Therefore, this paper proposed a method using insulator-based DEP (iDEP) devices to measure dielectric characteristics not only for negative DEP but also for positive DEP in a single cell. In the iDEP device, HEK293 (Human Embryonic cells 293) were observed to move in positive and negative DEP along with the center line of the device (Fig.2). Insulator-based DEP devices are expected to be a major tool for single-cell analysis because they are inexpensive and can measure both positive and negative DEP.

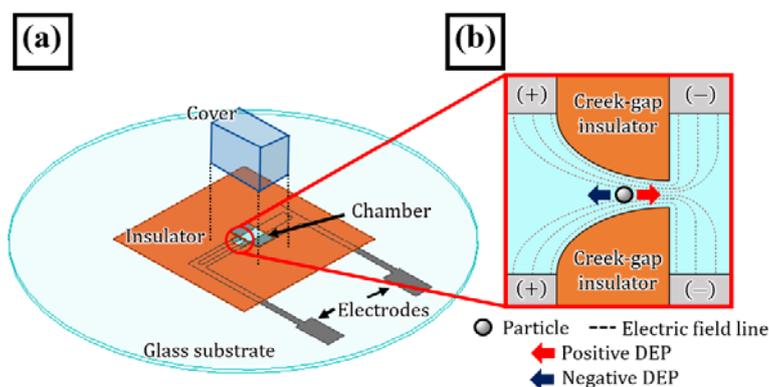


Fig. 1

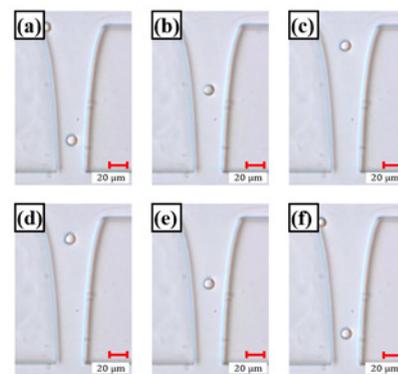


Fig. 2

Fig. 1: Illustrations of iDEP creek-gap device. (a) The isometric view of entire device. (b) The enlarged top view of the chamber.

Fig. 2: Dielectrophoresis of HEK293 cell. (a, b, c) Negative DEP. (d, e, f) Positive DEP.

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Aiming for metasurfaces by DNA-assisted lithography

J.M. Parikka¹, K. Tapio^{1,2}, J.J. Toppari¹

¹ Nanoscience Center and Department of Physics, 40014 University of Jyväskylä, Finland

² Department of Neuroscience and Biomedical Engineering, 00076 Aalto University, Finland

In a past decade, DNA origami has become one of the most used building blocks in self-assembled materials in nanoscale [1]. Using origami as tiles, large 2D lattices have been assembled with different techniques [2]. In our recent work, we have demonstrated that within certain ionic conditions the blunt-ended Seeman Tile [3] origami forms ordered 2D lattices [4] on top of silicon, as shown in figure 2b inset. These can be further utilized in lithography processes, like in DNA assisted lithography (DALI) [5] shown in figure 1. Our final goal is to fabricate a layered metamaterial surface like the one shown in figure 2a [6] but in smaller scale.

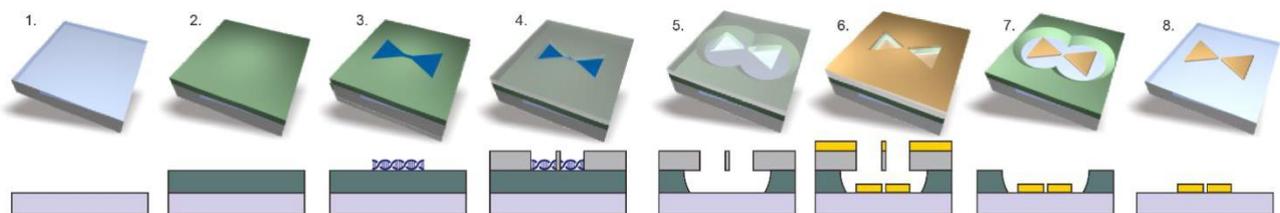


Fig. 1. DALI fabrication steps [5]: 1. Transparent substrate, 2. Silicon growth by Chemical Vapor Deposition, 3. Origami deposition, 4. SiO₂ growth by the special CVD, 5. Isotropic Si etching by Reactive Ion Etching (RIE), 6. Au depositions by evaporation, 7. Lift-off by HF:HCl wet etching, 8. Removing of Silicon by RIE.

We have already successfully demonstrated the DALI up to step 4, *i.e.*, we have selectively grown silicon dioxide around our DNA lattice [5] shown in figure 2b. The next step is to etch silicon layer all the way to the substrate using the SiO₂ layer as a mask. We have been optimizing the process with larger electron beam lithography (EBL) structures (figure 2c), which we have optimized so that the etching profile is easily visible. We require a high precision etch process with as large as possible Si/SiO₂ selectivity and anisotropic etch profile (no undercut) to avoid the collapse of the SiO₂ mask. Therefore, the etch is done in cryogenic temperatures using Ar, SF₆ and O₂ as precursors. Next step is to use etched pattern as an evaporation mask to make the metallic nanostructures.

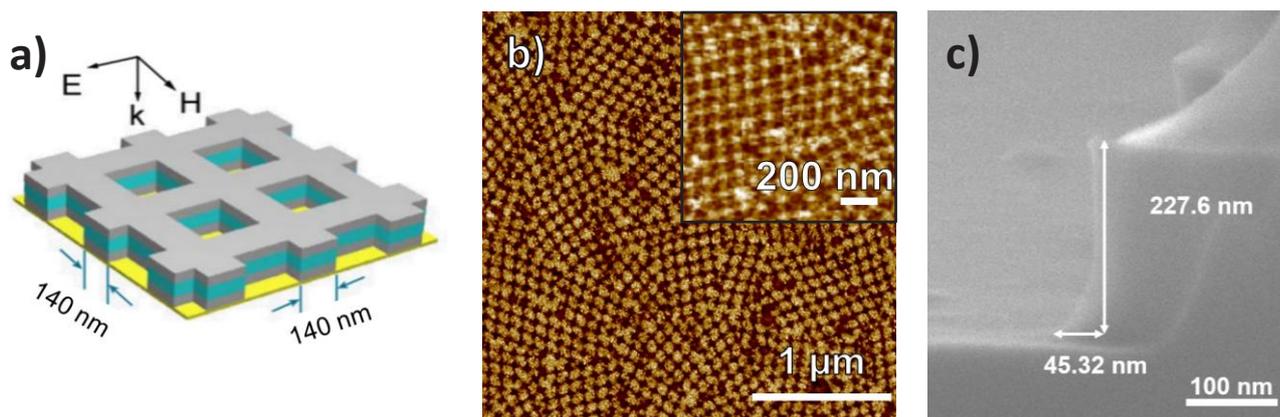


Fig. 2: a) Scheme for final structure [6] b) Surface after SiO₂ growth, origami lattice as inset on top right c) SEM image for one EBL sample etch profile.

[1] F. Hong, F. Zhang, Y. Liu, et al., *Chem. Rev.* 117, 12584-12640 (2017).

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[3] W. Liu, et al., *Angew. Chem. Int. Ed.* 50, pp.264-267 (2011) ; A. Rafat, et al., *Angew. Chem. Int. Ed.* 53, 7665–7668 (2014).

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[5] B. Shen, V. Linko, K. Tapio, et al., *Sci. Adv.* 4, p.eaap8978 (2018).

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Nanoantenna Conjugated Graphene Photodetectors

Abhinav Raina, Mo Lu, Max Reimer, Vasilii Osipov, Klaus Meerholz, and Klas Lindfors

Department für Chemie, Universität zu Köln, Greinstraße 4-6, 50939, Köln, Germany

Optical communications is a technology that utilizes light for the wireless transduction of signals. While initially envisaged as a future replacement for cable based communication systems, optical communications have begun to show promise in short range wireless communication. The rapid growth of nanoscale fabrication techniques has allowed for a significant improvement in the quality and reproducibility of the development of nanoscale structures required for the transduction of optical signals.

In their 2014 study, Dregely *et al.*^[1] have visualized the radiation pattern of optical nanoantennas as steerable wireless links by virtue of fluorescent molecules embedded in a polymer layer around the nanoantenna arrays. The resultant radiation pattern could be tuned by altering the polarization and position of radiation incident on the nanoantenna arrays, as well as the number of antennas in the array. In an effort to detect the signals generated by such optical nanoantenna links as an electrical signal, we couple nanoantenna arrays with a graphene photodetector.

In the development of our device we utilize an alternative strategy of placing the graphene above a layer of patterned electrodes and antenna which significantly improves the reproducibility of our fabrication process. We measure the dependence of the observed photoresponse on the aforementioned factors affecting the radiation pattern of the nanoantenna arrays. Such a device would act as a demonstration of tunable, on-chip wireless transmission and detection of optical signals.

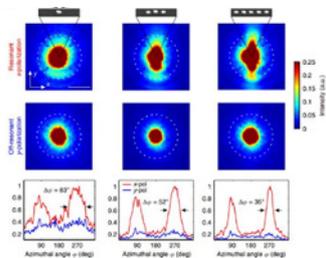


Fig. 1

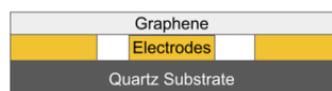


Fig. 2

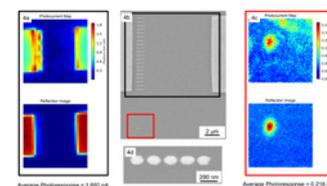


Fig. 3

Fig. 1: Radiation pattern of wireless nanoantenna links observed by Dregely et al. Figure taken from Ref. 1.

Fig. 2: Alternate device layout used in our approach

Fig. 3: Observed photoresponse from electrodes and nanoantenna arrays

[1] Dregely *et al.* (2014) *Nat Commun*, 5, 4354

Optimizing Photothermal Therapy for Cancer Treatment using Scuff-EM and K-Wave Simulations

Angelo Abraham Sanz ¹, Mateo Zutta ², Adriana De Mendoza ², César A. Herreño-Fierro ¹.

¹ Universidad Distrital Francisco José de Caldas, Faculty of Sciences and Education

² Pontificia Universidad Javeriana, Physics Department

Photothermal therapy (PTT) is a promising cancer treatment approach that utilizes near-infrared (NIR) light-absorbing (plasmonic) nanoparticles to generate heat, which in turn has the potential to destroy cancer cells. PTT has several advantages over traditional cancer therapies, such as chemotherapy and radiation therapy, including lower toxicity and higher specificity. To optimize the efficacy of PTT, it is important to understand the heat transfer process from the nanoparticle to the surrounding tissue.

We present preliminary results regarding the spatiotemporal distribution of the heat generated and delivered by the nanoparticle into the surrounding environment. To this aim, we use *Scuff-em*, a simulation tool for plasmonic processes, to obtain the optical response of a gold nanoparticle under NIR laser irradiation. The simulation results provide information about the absorbed power and the electric field distribution around the nanoparticle.

To further investigate the heat transfer process, we use *k-wave*, a *Mathlab* simulation tool, to obtain the temperature map around the nanoparticle. By combining these results, we gain a detailed understanding of the heat transfer process from the nanoparticle to the surrounding tissue.

Our preliminary results have potential implications in the design of PTT treatment protocols, allowing the control of the temperature distribution by optimizing nanoparticles' size and laser parameters. Once the temperature distribution is controlled, different cellular components or proteins can be targeted for therapeutic purposes, improving the treatment outcome and minimizing the damage to the healthy tissue. Overall, our approach provides a valuable tool for investigating the effectiveness of PTT and designing personalized cancer treatment protocols.

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Bi-metallic and nano-porous particles fabricated by pulsed UV laser irradiation for plasmonic sensing

Gabriele Schmidl¹, Marc Raugust^{2,1,*}, Guobin Jia¹, Frank Schmidl², Jan Dellith¹, Jonathan Plentz¹

¹ Leibniz Institute of Photonic Technology, Albert-Einstein-Straße 9, 07745 Jena, Germany; gabriele.schmidl@leibniz-ipht.de

² Friedrich Schiller University Jena, Institute of Solid State Physics, Helmholtzweg 5, 07743 Jena, Germany

*currently at: Pulsar Photonics GmbH, Kaiserstraße 100, 52134 Herzogenrath, Germany

Metallic nanoparticles (MNP) which are composed of different chemical elements and exist partially or only in the mixed phase under certain manufacturing conditions are very interesting materials for application areas in biophotonics or photocatalysis, among others. A mixing of metals, e.g., of Ag-Au, Ag-Cu, Pd-Au, or Ag-Pd, changes the material-dependent properties of pure element MNP and expands their potential applications.

These compound nanoparticles can be converted into inert nano-porous particles by dissolving out the less noble metal. Nanoporous, high-surface-area noble MNP with a low density are highly attractive for applications in photocatalysis, sensing, plasmonics, biochemistry, medical diagnosis, and are an excellent carrier platform to deliver therapeutic agents to tumoral tissues owing to their unique chemical and optical characteristics.

The basic nanoparticle manufacturing process is a laser process that brings nm layers into the melt and thus determines the mixture of materials in each particle. The particle formation process and thus the structural and optical properties of these particle surfaces are defined by the energy density and number of laser pulses, but also by the layer thicknesses of the total and individual layers and the substrate material. The defined very short heating and solidification process is characterized by a possible heat input from heating, through melting, to ablation and a very fast cooling process that suppresses phase separation. Transparent low-cost glass substrates can be used since the substrate is only low affected during this very fast process.

A defined array of porous inert structures and the use for nonlinear photonic effects will be targeted in future work.

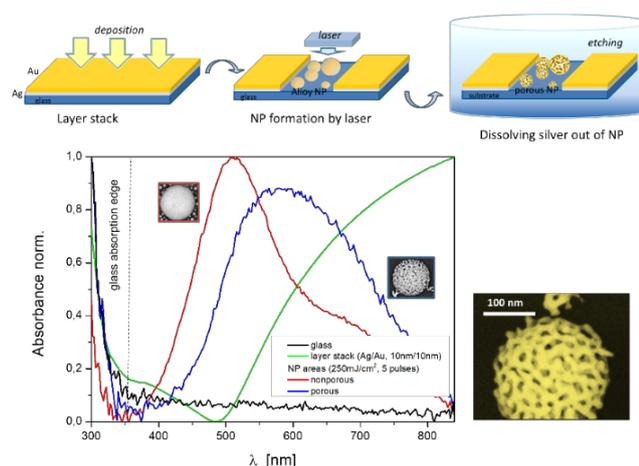


Fig. 1: **Top:** Sequence of the process to fabricate porous NP, **bottom:** Absorbance/resonance spectra of a layer stack Ag/Au (10/10nm – green curve) in comparison to laser treated areas (250 mJ/cm², 5 pulses) with nonporous NPs (red curve) and with porous NPs (blue curve), magnified illustration of a porous NP [4].

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[3] G. Schmidl et al. (2020). *Materials Today Communications*, 25, 101141.

[4] G. Schmidl et al. (2022). *Nanoscale Adv.* 4, 4122.

Ultrafast spatiotemporal chiroptical response of dielectric and plasmonic nanoparticles

Ankit Kumar Singh^a, Thomas Mayerhöfer^{a,b} and Jer-Shing Huang^{a,b,c,d,e}

a. Leibniz Institute of Photonic Technology, Albert-Einstein-Straße 9, 07745 Jena, Germany

b. Institute of Physical Chemistry, Friedrich-Schiller-Universität Jena, D-07743 Jena, Germany.

c. Abbe Center of Photonics, Friedrich-Schiller-Universität Jena, D-07743 Jena, Germany.

d. Research Center for Applied Sciences, Academia Sinica, Taipei 11529, Taiwan.

e. Department of Electrophysics, National Yang Ming Chiao Tung University, Hsinchu 30010, Taiwan

The study of nanostructure-enhanced chiroptical light-matter interactions is progressing towards the detection of chiral molecules at ultralow concentrations and ultrafast time scales. The understanding of the temporal response of the chiral molecule, the spatiotemporal response of the nanostructure and response of molecules in presence of the nanostructure becomes important for the determination of the molecular chirality and quantitative estimation of the chirality parameters.

Using Mie theory and the finite difference time domain method, we theoretically study the spatiotemporal response of a dielectric (silicon) and plasmonic (silver) nanosphere for an ultrashort pulse excitation (see Fig.1a). We show that while the optical chirality enhancement (OCE) by plasmonic spheres requires the presence of the incident (the pulsed excitation) and scattered fields, dielectric nanospheres can provide OCE even after the incident light (excitation) completely vanishes as long as the dielectric NPs support resonant electric (a_1) and magnetic (b_1) modes. The OCE in the scattered field of the dielectric particle is observed due to the interference of the fields of electric and magnetic modes (see Fig.1b). We further demonstrate spectral tuning of the spatial distribution of OCE by controlling the phase between the electric and magnetic resonant modes in a dielectric nanosphere.

The work highlights the understanding and manipulation of the ultrafast and nanoscale spatiotemporal evolution of the near-field OCE around resonant nanospheres excited by fs-pulsed excitation and may find applications in spatiotemporal control of the chiroptical response of nanostructures.

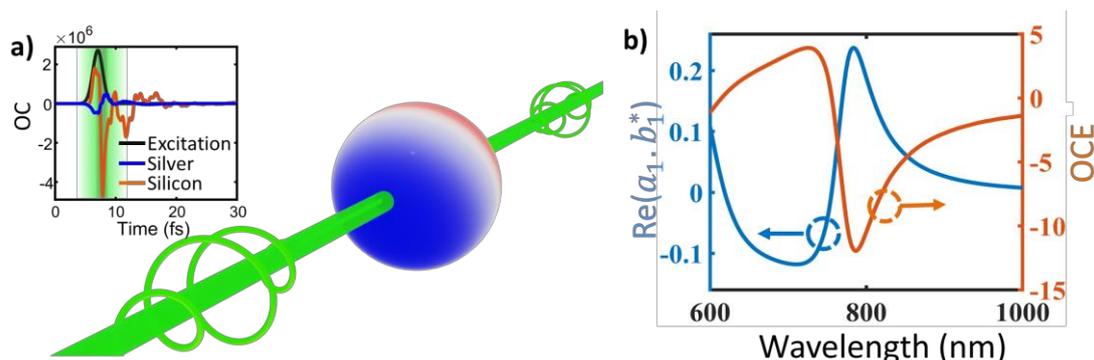


Fig. 1: a) A schematic showing an ultrafast optical illumination of a nanosphere and near field optical chirality (OC). The time-dependent OC in the scattered field for the silicon and silver nanospheres is shown in the inset. b) The effect of electric (a_1) and magnetic (b_1) dipole mode interference (blue, left axis) on the OCE spectrum (red, right axis) obtained at a point in the equatorial plane for silicon nanosphere.

[1] Polavarapu P L. *Chiral analysis: advances in spectroscopy, chromatography and emerging methods*. 2018.

[2] Ayuso D, Ordonez A F, and Smirnova O. *Ultrafast chirality: the road to efficient chiral measurements*. PCCP. 2022; 24: 26962-26991.

SERS probing of endolysosomes with gold nanostars

Cecilia Spedalieri, Janina Kneipp

Department of Chemistry Humboldt-Universität zu Berlin, Brook-Taylor-Str. 2, 12489, Berlin, Germany

Gold nanostars are anisotropic structures with interesting plasmonic properties that have potential for a wide range of theranostic and biophotonic applications. It is relevant to understand how these nanostructures interact with biomolecules inside living cells and what conditions may affect these interactions. The use of surface enhanced Raman scattering (SERS) spectroscopy allows for label-free detection of these biomolecules revealing information on nanostructure-biomolecule interactions,[1] and combined with other techniques may provide a more complete picture of nanoparticle processing by cells.[2,3]

In this work we present the results of probing the endolysosomes of living cells of three different cell lines with gold nanostars via SERS.[2,3] The biomolecule-nanostar interactions occur mainly through protein components (Fig 1), and distinctive features can be observed for the different cell lines. Distinctive SERS signals are also found at different incubation times, reflecting the different stages of endolysosomal processing of the nanostars. Nanostars with different spike length interact differently with hydrophobic components in endolysosomes regardless of the cell line they reside in. Furthermore, their optical properties differ, as demonstrated in experiments and FDTD simulations of the electromagnetic enhancement.[2] Information on the distribution of gold nanostar aggregates inside the cells was obtained with synchrotron soft X-ray tomography (SXT), showing that their localization, size, and density vary with cell line and incubation time.[3]

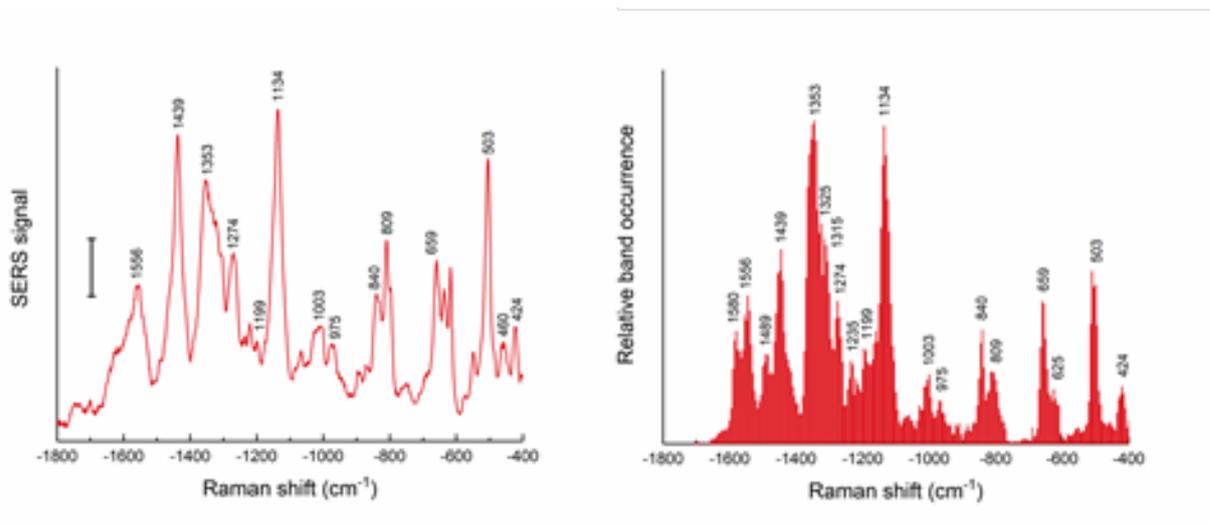


Fig. 1: SERS spectrum (left) and frequency of occurrence (right) for 3T3 cells incubated for 24 h with gold nanostars of short spike length

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Optical waveguide (OW) biosensor

[Keiji Tada](#), Takeshi Kawajiri, Shoichiro Kaji

FURUNO ELECTRIC CO.,LTD., 8-1 Jingikan-cho, Nishinomiya, 662-0843, Japan

We are researching and developing a simple and rapid immunoassay device using the optical waveguide (OW) biosensor. SPR (Surface Plasmon Resonance) is generally used as a label-free biomolecular interaction detection method. We compared the FOM (Figure Of Merit) of the OW biosensor and the SPR biosensor by simulation, and confirmed that the OW biosensor has several tens of times the FOM of the SPR biosensor.

We report the design of the OW biosensor by simulation and the demonstration by optical experiments.

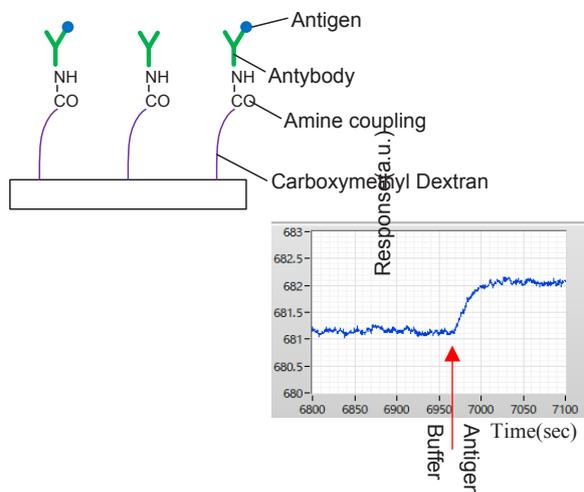
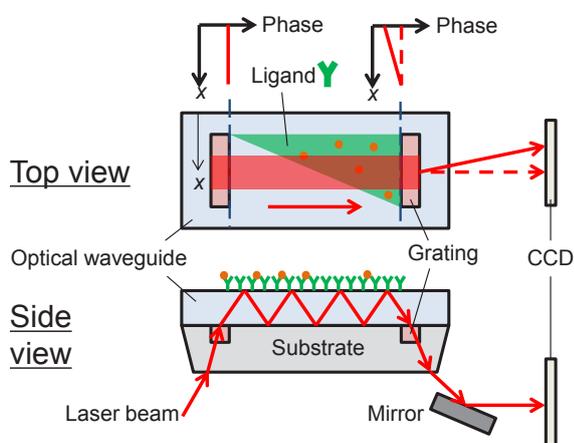


Fig. 1

Fig. 2

Fig. 1: Principle of OW biosensor

Fig. 2: Response of antigen-antibody reaction

Near-Infrared Luminescent Platinum Nanoclusters for *in vivo* Imaging and Biomedical Application

[Shin-ichi Tanaka](#)¹, [Hirohiko Niioka](#)², [Hiroki Wadati](#)³

¹National Institute of Technology, Kure College, 2-2-11 Agaminami, 737-8506 Kure, Japan

²Institute for Dataability Science, Osaka University, 2-8 Yamadaoka, 565-0871 Suita, Japan

³Graduate School of Material Science, University of Hyogo, 3-2-1 Kouto, Kamigori-cho, 678-1297 Ako-gun, Japan

Biomedical imaging has become an indispensable tool in the fields of cancer diagnosis and therapy. Particularly, near-infrared (NIR) fluorescence biomedical imaging can reduce tissue autofluorescence and scattering and can improve efficiently and harmlessly the tissue penetration depth for *in vivo* application. Our recent studies demonstrated that NIR-emitting platinum (Pt) nanoclusters possessed low cytotoxicity, ultrasmall size, excellent photostability, and high brightness, and could be utilized as a fluorescent probe for highly sensitive optical imaging of cancer on both the cellular and the animal level. The NIR-emitting Pt nanoclusters were synthesized by using PAMAM dendrimers as molecular templates. The synthesized Pt nanoclusters exhibited from red to NIR emission ($E_m = 630$ to 820 nm) and possessed approximately 1% quantum yield. (Fig. 1) After conjugating the Pt nanoclusters with PAR-1 (Protease-Activated Receptor 1) antibody, we labeled the MDA-MB-231 cells (breast cancer) and obtained the fluorescent image of single living cells. (Fig. 2) Finally, we performed *in vivo* tumor imaging using PAR-1 conjugated Pt nanoclusters. Owing to the expression of PAR-1 in breast cancer cells, Pt nanoclusters preferentially bounded on the surface of breast cancer cells and can effectively be accumulated tumor tissues. Our NIR luminescent Pt nanoclusters promise to be a useful fluorescent probe for *in vivo* imaging and biomedical application.

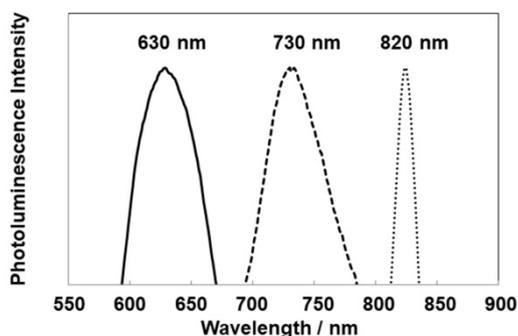


Fig. 1

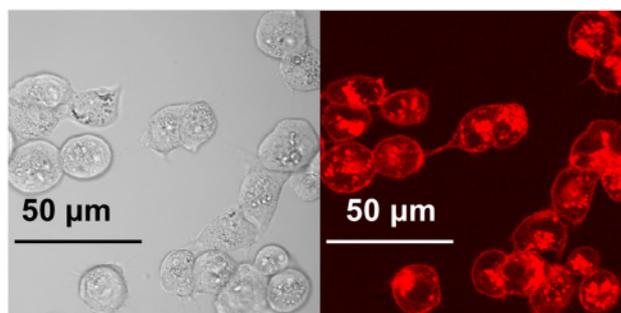


Fig. 2

Fig. 1: The luminescence spectra of the synthesized red to NIR emitting Pt nanoclusters

Fig. 2: Brightfield (left) and confocal luminescence (right) images of living MDA-MB-231 cells incubated with PAR-1 conjugated red-emitting Pt nanoclusters

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[3] S. Tanaka et al. (2011). *Angew Chem Int Ed*, 50, 431-435.

On the Road from Top-down to Bottom-up by DNA-Assisted Lithography

Kosti Tapio^{1,4}, Charlotte Kielar², Johannes Parikka¹, Adrian Keller³, Heini Järvinen¹, Anton Kuzyk⁴, Karim Fahmy², Jussi Toppari¹

¹Department of Physics and Nanoscience Center, University of Jyväskylä, 40014 Jyväskylä, Finland.

²Institute of Resource Ecology, Helmholtz-Zentrum Dresden-Rossendorf (HZDR), 01328 Dresden, Germany.

³Technical and Macromolecular Chemistry, Paderborn University, 33098 Paderborn, Germany.

⁴Department of Neuroscience and Biomedical Engineering, Aalto University, 00076 Aalto, Finland.

Crafting plasmonic substrates, especially hierarchical that can be used as metamaterials, has garnered interest over the past decades [1,2]. One of the more promising plasmonic structures is the fishnet-type lattice (Figure 1a), where the coupling between two separated metal layers can induce negative refractive index at certain wavelengths [3]. Such lattices have been fabricated using electron beam and photolithographies, but our aim is to utilize bottom-up based techniques like DNA-assisted lithography (DALI) [4] instead since it offers cost-effective, parallel, and possibly simpler method of fabrication, that can be scaled up to a wafer size.

In our work, a cross shaped DNA origami called Seeman Tile (ST) [5,6] was utilized to form fishnet-type lattices on a silicon substrate in dry conditions (Figure 1b, left image). Initially, we investigated the effects of different buffer conditions, temperature, and DNA origami design on the formation of the DNA origami lattice by AFM in liquid. These findings were then used as a basis to develop the final deposition protocol and transfer the sample to dry state. Finally, the capability of our DNA origami lattice to act as a mask in silica chemical vapor deposition process was tested resulting in a well-defined lattice shaped openings and a uniform silica layer (Figure 1b, right image). This silica layer can be further utilized in DNA-assisted lithography as a physical vapor deposition mask to form the layered, metal-oxide fishnet structures.

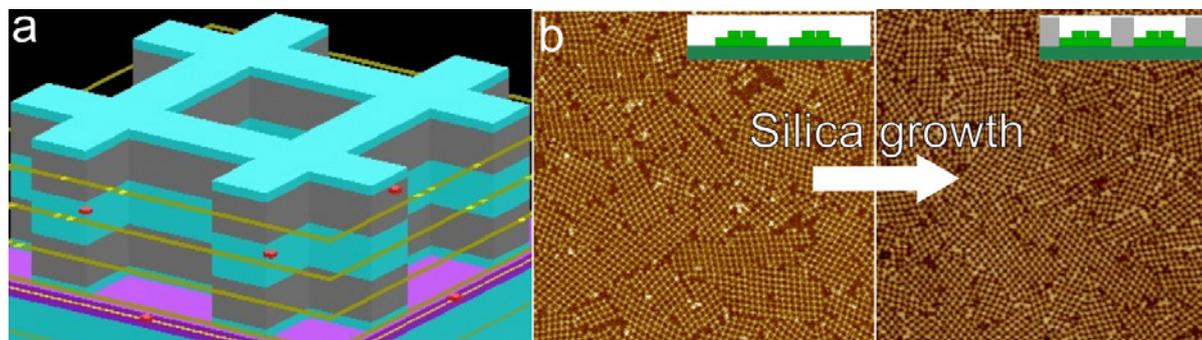


Fig. 1. (a) Schematic view of a multilayered fishnet-type lattice. The multilayered structure consists of insulating Al_2O_3 (green) and conductive Ag (grey) layers. (b) On left, AFM image of Seeman Tile fishnet-type lattice deposited on a silicon substrate. On right, a similar DNA lattice after silica growth, where origami shaped holes can be observed.

[1] J.B. Pendry (2000). *Phys. Rev. Lett.*, 85, 3966-3969.

[2] Z. Wang, F. Cheng, T. Winsor, Y. Liu. (2016). *Nanotechnology*, 27, No. 412001.

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[4] B. Shen, V. Linko, K. Tapio, S. Pikker, T. Lemma, A. Gopinath, K.V. Gothelf, M.A. Kostianen, J. Toppari (2018). *Sci. Adv.*, 4, eaap8978.

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[6] A.A. Rafat, T. Pilzer, M.B. Scheible, A. Kostina, F.C. Simmer (2014). *Angew. Chem. Int. Ed.*, 53, 7665-7668.

Controlling the selective adsorption of plasmonic DNA origami nanostructures using polar surface arrays

Z. Wang^{ab}, Z. Liu^{bc}, S. Kogikoski^d, I. Bald^d, R. Stosch^a, S. Wundrack^{ab}

a) Physikalisch-Technische Bundesanstalt, Bundesallee 100, 38116 Braunschweig, Germany

b) TU Braunschweig LENA, Langer Kamp 6a/b, 38106 Braunschweig, Germany

c) TU Braunschweig Institut für Angewandte Physik, Mendelssohnstraße 2, 38106 Braunschweig, Germany

d) Universität Potsdam Institut für Chemie, Karl-Liebknecht-Straße 24-25, 14476 Potsdam, Germany

The detection of specific single molecules in liquids, adsorbed on surfaces or in the gaseous state, is a long-desired goal in spectroscopy and requires spectroscopic techniques offering high spectral sensitivity. Surface-enhanced Raman spectroscopy (SERS) is one of these techniques that has been significantly developed in recent decades and now has the potential to detect the spectroscopic fingerprint of individual molecules using plasmonic-active materials. The gain of spectral sensitivity in SERS can be achieved by utilizing DNA origami structures with plasmonic metal nanoparticles, forming complex nanostructures for SERS detection. However, such measurements are challenging since the nanostructures easily agglomerate when attached to surfaces.

Here, we introduce a promising approach to precisely control the adsorption position of DNA origami nanostructure on a flat substrate in the form of a polar surface array (PSA). The PSA surface is fabricated by physical vapor deposition (PVD) of specific organic molecules on a hydrophilic substrate, followed by electron-beam lithography (EBL) for surface patterning with nanometer precision. AFM and XPS were applied to study the surface properties of the PSA after chemical functionalization. Furthermore, our results demonstrate that the polar surface pattern of the PSA substrate drastically reduces the agglomeration of DNA nanostructures, as shown by scanning electron microscopy (SEM) studies. Finally, we have analyzed the adsorption efficiency of DNA nanostructures on PSA by considering the Langmuir isotherm, whereas the bonding states at the DNA/substrate interface have been confirmed by the DFT simulation.

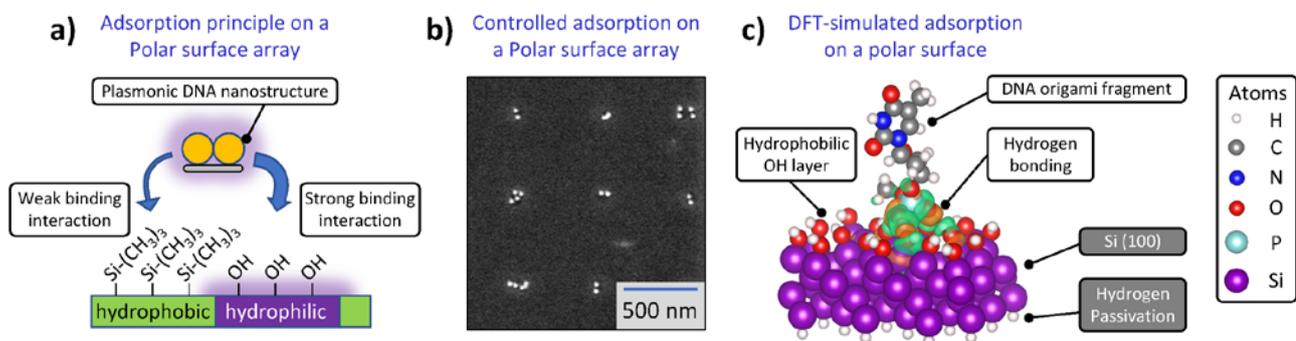


Fig. 1: a) Proposed adsorption behavior of plasmonic DNA nanostructure on a Polar surface array (PSA). b) SEM measurement of deposited nanostructures on a PSA substrate. (c) DFT-simulated adsorption of a DNA origami fragment on hydrophilic Si (100) surface. The hydrogen bonding is indicated by the charge density difference, which is represented by orange (electron density accumulation) and green (electron density depletion) clouds, respectively.

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Meta-devices for 6G applications and beyond

Jing Cheng Zhang, Yao Liang, Din Ping Tsai

Department of Electrical Engineering, City University of Hong Kong, Kowloon, 999077, Hong Kong.

Meta-lenses are a high potential for future applications of the sixth-generation (6G) communication network [1,2]. Meta-lenses could help enhance the transfer directivity and the signal's concentration strength, critical points of the 6G generation technology. A traditional terahertz communication system usually has bulky and complex setups, especially dielectric lenses and reflectors. They are the elements to guide the terahertz waves into transmitters or focus the incident beams to the detector [3]. However, these elements lose flexibility and can only guide the waves to a transmitter or a receiver in a fixed location or cover a limited area hindering the future development of the 6G applications [4].

Here we report a novel terahertz meta-lens to manipulate the focal spots with a fully tunable range [5]. The different setups for the meta-lens guide the focal spot to various transmitters or detectors, providing a massive promotion for a flexible, high directivity, high signal concentration, and a future secure 6G communication system. Besides the free regulation of the varifocal characteristics, the diffraction-free, self-healing, self-accelerating properties of Airy beams can also improve the stability and security of the signal in future 6G communication systems. This meta-lens technology avoids the high costs related to numerous use of components like pin diodes and varactor diodes. It will benefit their large-scale deployments in the 6G communication systems, wireless power transfer, zoom imaging, and remote sensing.

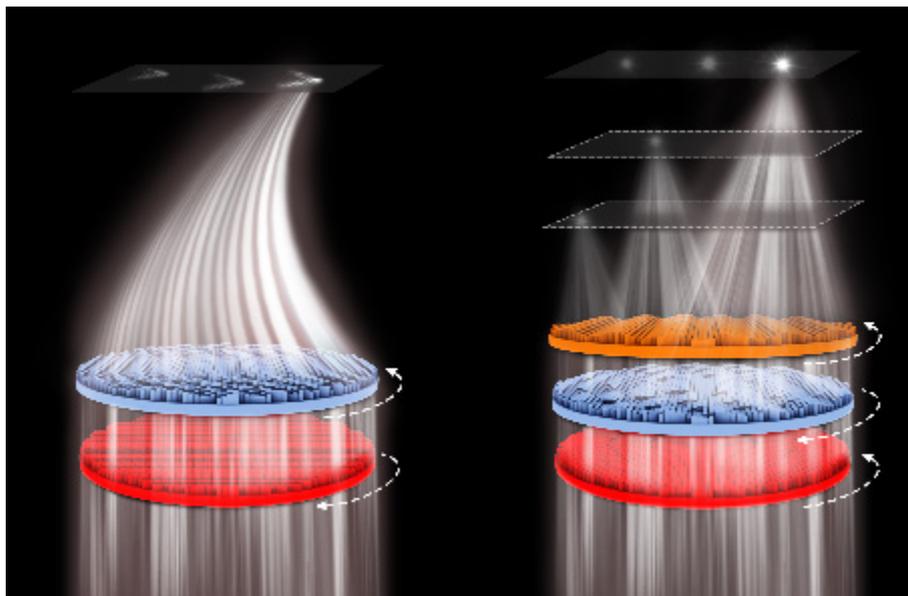


Fig. 1 The schematics of the varifocal meta-devices

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Monitoring Photolipid Bilayer Membrane Switching with Plasmonic Nanorods

Jinhua Zhang, Dominik Kammerer, Francis Schuknecht, Ludwig Habermann, Alexander Patts, Stefanie D. Pritzl, Theobald Lohmüller

Chair for Photonics and Optoelectronics, Nano-Institute Munich, Department of Physics, Ludwig-Maximilians-Universität, Königinstraße 10, 80539 Munich, Germany.

Photoswitchable lipids (named photolipids) are highly effective tools to control the physical properties of lipid bilayer membranes with light. [1-4] However, analyzing the switching dynamics in a single bilayer locally and *in situ* is challenging due to a lack of sensitive tools for monitoring the very small changes in lipid conformation and membrane thickness (< 1 nm). Here, we demonstrate a new approach to analyze the photoisomerization of photolipid membranes on the nanoscale via plasmonic sensing.

We devised an experiment, where gold nanorods are deposited on a glass substrate and coated with a supported photolipid bilayer (SPB). The photosensitive azobenzene group in the lipid tails is switched between a *trans* and *cis* form with UV (365 nm) and blue light (465 nm), while the dark-field scattering spectra of individual nanorods are simultaneously measured. We find that lipid photoisomerization leads to a shift of the nanorod's plasmon resonance that is reversible over many switching cycles. Furthermore, we show that the corresponding photoisomerization dynamics of SPBs can be analyzed with high accuracy by time-dependent measurements of the plasmon resonance shift.

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