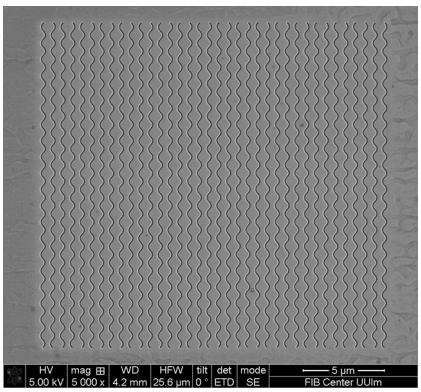
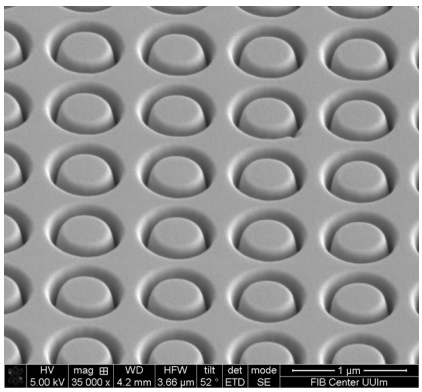
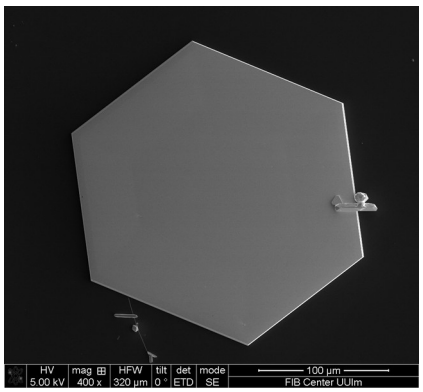
Workshop

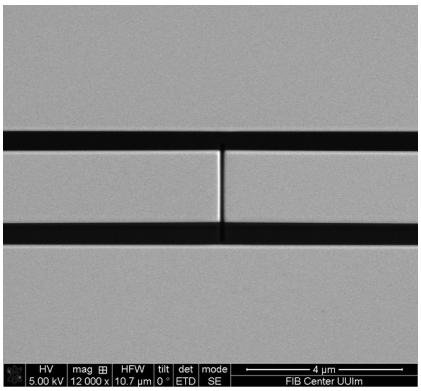
“Plasmonic Resonators and Applications”

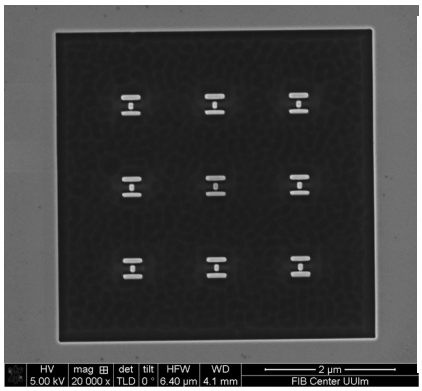
Ulm University, Germany, 4-5 July 2019

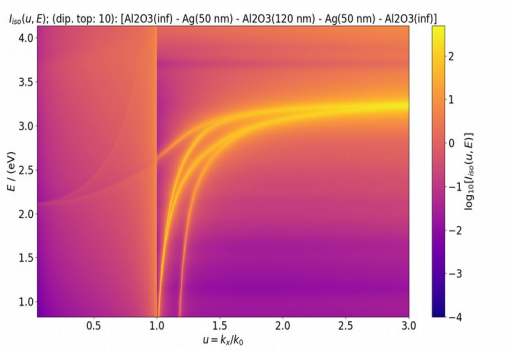












Room: Universität Ost, O29/3002

Organizers:
Manuel Gonçalves – Ulm University, Germany
Hayk Minassian – Yerevan Physics Institute, Armenia
Armen Melikyan – Russian-Armenian University, Armenia

Support:

BMBF

Ulm University

Ministry of Education and Science of Armenia

Min. of Educ. and Science of Armenia, Science Committee

Topics:

Optical resonances in plasmonic nanoparticles
Plasmonic cavities
Metasurfaces and metamaterials
Nonlinear plasmonics
Applications in biophysics and biology
Plasmonic sensors
Interaction between electron beams and plasmons
Quantum plasmonics

Venue: Building East, O29/3002 (see location in map)

The room is equipped with video projector and board.

Social event:

After the workshop on Friday 5th July afternoon there will be a grill party at the Institute of Experimental Physics in N25 / 5th Floor.

SCIENTIFIC PROGRAM

Thursday, 4th July

14:00 Workshop opening

14:10 *"An Overview of Plasmonic Resonators"*
Dr. Manuel Gonçalves, Inst. of Experimental Physics - Ulm University, Ulm, Germany

15:00 Invited Talk: *"Mechanisms of Electromagnetically Enhanced Raman Scattering"*
Dr. Armen Melikyan, Russian- Armenian University, Yerevan, Armenia

16:00 *"Tunable Nanoplasmonic Substrates for Biosensory Applications"*
Peter Kolb, Inst. of Experimental Physics - Ulm University, Ulm, Germany

16:30 "*A photonics platform based on silicon vacancy centers in diamond and a fiber cavity"*
Stefan Häußler, Inst. of Quantum Optics - Ulm University, Ulm, Germany

16:45 *"Efficient Coupling of an Ensemble of Nitrogen Vacancy Center to the Mode of a High-Q, Si_3N_4 Photonic Crystal Cavity"*
Konstantin Fehler, Inst. of Quantum Optics - Ulm University, Ulm, Germany

Friday, 5th July

9:30 Invited Talk: "*Nonlinear plasmonics: materials, structures and optical modes"*
Prof. Olivier J. F. Martin - École Polytechnique Fédérale de Lausanne (EPFL), Switzerland

10:30 Invited Talk: *"Spin-photon interface of SiV^- center in nanometer-sized diamond host"*
Prof. Alexander Kubanek, Inst. of Quantum Optics - Ulm University, Ulm, Germany

11:30 - 13:00 Lunch

14:00 Invited Talk: *"Nano-optics of Surface Plasmon with Electron Beam: Cathodoluminescence Study"*
Dr. Achyut Maity, Max-Planck Institute for Solid State Physics, Stuttgart, Germany

15:00 Invited Talk: *"Two-dimensional titanium carbide (MXene) as surface-enhanced Raman scattering substrate"*
Dr. Hayk Minassian, A. Alikhanian National Lab, Yerevan, Armenia

From 16:30 on: Meet together at the Institute of Experimental Physics. Drinks, foods, grill

An Overview of Plasmonic Resonators

Manuel Gonçalves[1]

[1] Ulm Universty, Ulm, Germay

The history of surface plasmons began with the theoretical article of Rufus Ritchie in 1957 [1]. The already known low energy losses in electron beams crossing thin metal films was already known experimentally, but its complete explanation was until then not clear. 11 years later Andreas Otto, and independently Heinz Raether and Erwin Kretschmann proposed the first setups for the excitation of surface plasmons [2, 3]. However, already in 1908 other related phenomenon, the colors of gold and silver colloidal solutions had already been described by the Mie theory [4]. Despite the fact that the Mie theory represented a huge progress in the explanation of colloidal particles resonances, only much later the association of these resonances with surface plasmons took place. The Mie theory is only applicable to perfect spheres and infinite cylinders. Approximations to the full theory have been used for the calculation of the scattering spectra and the near-fields of ellipsoids and spheroids [5]. The optical resonances in small particles are not exclusive of noble metal particles. Indeed, more recently the investigation of magnetic multipolar resonances in spherical particles of large refractive index has deserved large attraction [6, 7, 8, 9, 10].

All the the optical resonances arising in individual particles depend on the particles shape and size, the dielectric function of the particles and the optical constants of the surrounding dielectric medium. But, other resonances arise in coupled systems. The near-field coupling of surface plasmon resonances in small nanostructures may lead to another kind of scattering and absorption: the Fano resonance [12, 13]. Fano resonances were firstly discovered in the context of atom optics. However, they are a much more universal resonant interaction with typical asymmetric lineshape.

More recently another kind of coupling has been investigated very intensively: the weak and the strong coupling between surface plasmons and light emitters [14, 15]. Strong coupling of a single atom with a single photon in a cavity has been a hot topic of quantum optics since the 80s of the last century. However, it is possible to observe the anti-crossing typical of strong coupling between surface plasmons and fluorescent emitters surrounding the metal surface.

Three other phenomena were either predicted and experimentally verified in the last 10 years and have had a profound impact in plasmonics: the excitation of toroidal resonances in plasmonic cavities [16], the hyperbolic metamaterials [17] and the optomechanical coupling between surface plasmons and vibrating membranes [18]. An overview (necessarily brief) of the topics will be presented.

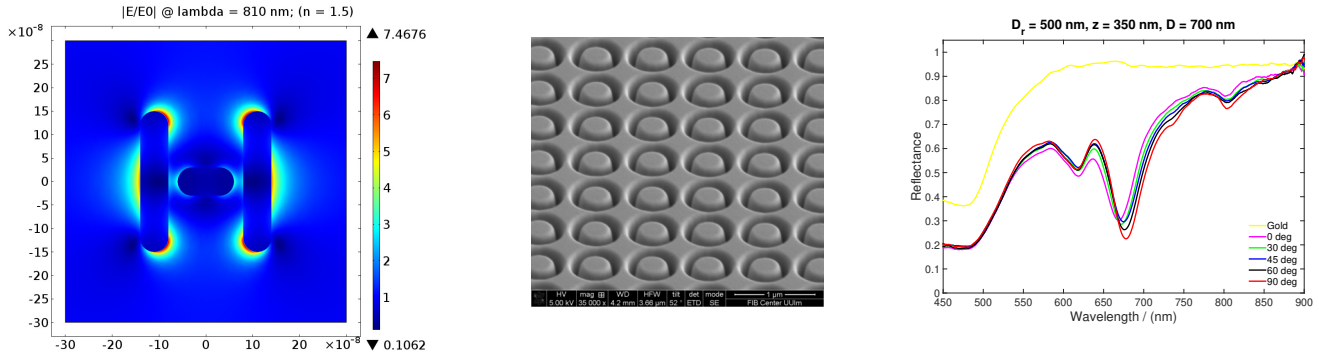


Figure 1: (Left): Near-field enhancement of coupled Au rods; (Center): Array of circular cavities fabricated by FIB in a crystalline gold plate; (Right): Reflectance of the circular cavities array for different polarization directions.

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Mechanisms of Electromagnetically Enhanced Raman Scattering

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Russian-Armenian University, Yerevan, Armenia

It is known that there are several electromagnetic mechanisms of SERS forming the enhancement factor. Here we introduce an analytical model to consider sources of enhanced Raman scattering and identify the contributions of different mechanisms in this effect. Developed approach allows realistic modeling for numerical calculations and interpretation of experimental data. Fore mechanisms of electromagnetically enhanced Raman scattering are considered: image dipole enhancement effect; increase of local field ("lightning rod" effect); resonant excitation of surface plasmons; resonant absorption in dye molecule. Different models for SERS were analyzed numerically [1, 2, 3] however they do not allow identification of the contribution of above-mentioned mechanisms in forming the SERS enhancement factor (EF).

We introduce analytical model to estimate the range of external field frequencies corresponding to maximum EF of SERS and to reveal and separate the contributions of different electromagnetic mechanisms of enhancement. To the best of our knowledge this is the first attempt to analyze the competition of mentioned above mechanisms of SERS based on clear and simple physical interpretations. Our model is based on the following assumptions: 1) Protrusions of metallic surface are modelled by nanospheroid, and analyte molecule is modelled as polarizable point dipole.

2) The distance between the dipole and the spheroid surface is assumed to be smaller than the curvature radius of the spheroid at the vicinity of its apex.

3) For description of image enhancement mechanism the spheroidal nanoparticle is replaced by the sphere with radius equal to the curvature radius of spheroid.

4) Validity of the model is justified by the comparison with the well - known numerical results.

Here we do not analyze "hot spot" enhancement effect since we consider only one metallic nanoparticle near the analyte molecule. This mechanism will be discussed separately while presenting our numerical results for two nanospheroids with the point dipole in between them. With these assumptions we obtain the following expression for SERS enhancement factor

$$\eta(\lambda, y) = \left| \frac{\dfrac{\epsilon(\lambda)}{[\epsilon(\lambda) - 1]\, L_0(\xi) + 1}}{1 - \dfrac{\epsilon(\lambda) - 1}{\epsilon(\lambda) + 1} \dfrac{\alpha(\lambda)}{8 y^3 \rho^3} (2 - y + y^2)} \right|, \tag{1}$$

where $\epsilon(\lambda)$ is the complex dielectric function of spheroid material, $\alpha(\lambda)$ is the complex polarizability of the molecule, $\xi = \sqrt{c^2/(c^2 - a^2)}$ with c and a being the major and minor semiaxes of the spheroid, $\rho = a^2/c$ is the curvature radius at the vertex of the spheroid, $y = h/\rho$ and h is the distance from the apex of the the spheroid to the dye molecule, and finaly

$$L_0(\xi) = (\xi^2 - 1) \left[\frac{\xi}{2} \ln \left(\frac{\xi + 1}{\xi - 1} \right) - 1 \right].$$

The calculation of (1) for silver nanospheroid located close to the point dipole with constant polarizability give the following dependence on SERS enhancement factor on the photon energy:

Red line on Fig. 1 is obtained from (1), the blue line is the same without image effect - $\alpha(\lambda) = 0$ mention that for the same values of the parameters red line agrees very well with exact solution of the problem of silver spheroid and point dipole with constant polarizability [1]. It is obvious that for the chosen parameters ($h = 0.5$ nm, aspect ratio $c/a = 5$, $\alpha = 0.01$ nm 3) the contribution of image effect is negligibly small. As our calculations show the increase of the polarizability of the analyte molecule by 5 times ($\alpha = 0.05$ nm^3) with the same values of other parameters increases the EF by the factor of 1.5. It is important to note, that the photon energy of 2.1 eV is very close to the plasmonic resonance of the silver nanospheroid with aspect ratio 5. Thus the obtained high value of $EF \sim 10^{11}$ is conditioned by resonant excitation of surface plasmons. If the point dipole possesses realistic frequency dependent polarizability, e.g. R6G dye molecule near the Ag nanospheroid, from (1) we obtain for $h = 0.5$ nm, aspect ratio $c/a = 5$ the value $EF = 10^{10}$. It is interesting however that for specially chosen parameters $h = 0.79$ nm, aspect ratio $c/a = 4.6$ we obtain from (1) extremely high value of $EF = 10^{18}$. This unusual enhancement is a result of coincidence of two frequencies plasmonic and eigenfrequency of the system molecule and its image corresponding to $\lambda_{res} = 587$ nm. It also follows from our consideration that when the incident frequency is far from plasmonic resonance the SERS is mostly conditioned by the lightening rod effect with $EF \sim 10^{10}$ as it is expected. In

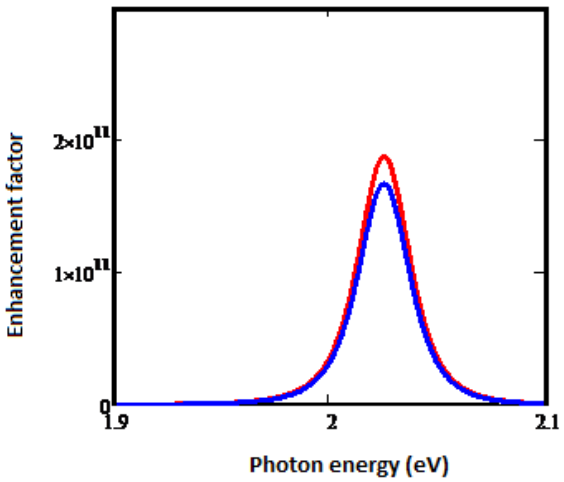

Figure 1: Dependence of SERS enhancement factor on the photon energy.

case of MXene substrate EF can reach the value of 10^6, which is close to observed data [4]. It is demonstrated that EF does not depend on aspect ratio, i.e. on the shape of nanoparticle. This peculiarity shows that SERS in MXene is conditioned by interband transitions causing lightening rod effect [4].

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Tunable Nanoplasmonic Substrates for Biosensory Applications

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Abstract

The physical interaction of a cell with its environment can be observed by tracking the substrate they are attached to. The stress a cell exerts on a substrate leads to a deformation which can be used to calculate cellular forces. Commonly used methods to track substrate deformation use markers, e.g. fluorophores, which have the disadvantage that the position of each marker needs to be continuously tracked. The use of plasmonic nanostructures promises to encode information about substrate strain in the transmission spectra and therefore the color, instead of tracking single particles.

Arrays of metallic nanoparticles show specific electromagnetic resonances which are strongly dependent on their geometry. Coupling between closely spaced plasmonic particles leads to a strong resonance dependence on the interparticle distance. By combining gold nanoparticles with a soft PDMS substrate, resonances can be mechanically tuned [1] or used to detect substrate strain [2].

We performed electromagnetic simulations to determine the reflectances and transmittances of different geometries and materials using COMSOL Multiphysics. Simulations revealed shifts in the resonance when the substrate is stretched (Figure 1).

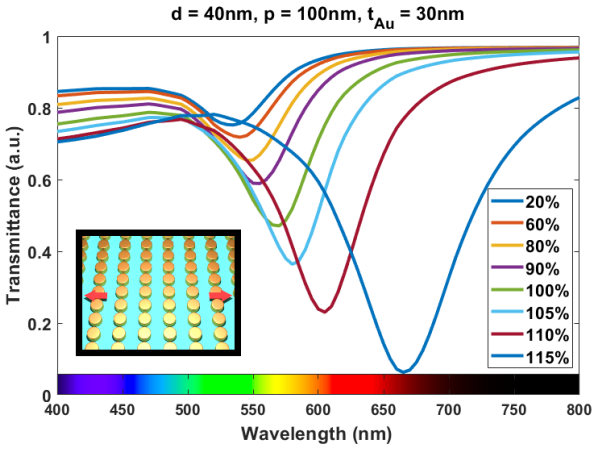

Figure 1: Simulated transmittances for a gold nanodisc array that is stretched from 20% to 115%. Inlet shows a depiction of the nanodisc array when stretched.

Utilizing electron beam lithography, electron beam evaporation, and lift-off procedures, we produced gold nanodisc arrays on soft Polydimethylsiloxane (PDMS) substrates. The transfer of gold discs from silicon to PDMS has the advantage that mechanical properties of the substrate are not changed. Instead of using chromium or titanium for adhesion, a mercaptosilane was used, which does not interfere with the plasmonic properties of gold.

Transmittance measurements revealed that the position of the plasmonic resonance coincides with the simulated spectra (Figure 2).

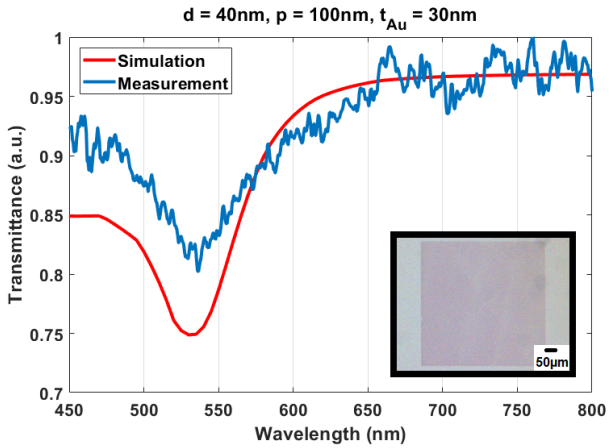

Figure 2: Comparison of measured and simulated transmittance of a gold nanodisc array. Inlet shows the color as seen through an optical microscope.

Further measurements need to be conducted to confirm the resonance shifts which are to be expected from simulations.

Acknowledgement

The authors wish to thank the members of the Institute of Electronic Devices and Circuits and the members of the Institute for Experimental Physics at Ulm University.

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A photonics platform based on silicon vacancy centers in diamond and a fiber cavity

Stefan Häußler[1,2,*], Richard Waldtrich[1], Gregor Bayer[1], and Alexander Kubanek[1,2]

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[2] Center for Integrated Quantum Science and Technology, Ulm University, University of Stuttgart and Max Planck Institute for Solid State Research, Germany
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Solid-state quantum emitters offer one promising platform for various quantum technology applications like quantum repeaters. Especially color centers in diamond, like the negatively charged nitrogen vacancy (NV^-) and silicon vacancy (SiV^-) center have been extensively studied due to its outstanding spin and optical properties. The SiV^- center possesses a high Debye-Waller factor (~ 0.7), exceptional spectral stability due to the inversion symmetry of the defect and a narrow inhomogeneous distribution. The remaining challenges are the low rate of coherent photons, the poor extraction efficiency out of the high refractive index host material and the low quantum yield.

In this talk I present a light matter interface based on a high quality fiber Fabry Perot microcavity and an ensemble of SiV^- centers in a thin (~ 200 nm), single crystal diamond membrane to overcome these challenges paving the way towards a scalable use in quantum technology applications. We show spectral funneling of the SiV^- ensemble emission into the cavity mode and further investigate the system towards scattering losses to estimate possible Purcell enhancement in high Q resonators.

References

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Nonlinear plasmonics: materials, structures and optical modes

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Abstract

Nonlinear optics is a fascinating topic of modern optics, which has been made possible by the developments of ultrafast lasers. Nonlinear optical phenomena usually resort to specific bulk crystals with a strong nonlinear susceptibility. In this talk, I will explore another way of realizing nonlinear optical effects, using plasmonic nanostructures. Such nanostructures do not exhibit a strong bulk nonlinear susceptibility; yet, they can be used to produce nonlinear effects, such as second harmonics that originate from the surface of the metal. The different mechanisms that lead to nonlinear effects in plasmonic nanostructures will be described and I will show how they can be enhanced by the strong near-field produced by plasmonic nanostructures and how the symmetry and the modes of the system control these nonlinear effects. The talk will not assume much knowledge about nonlinear optics and introduce the different concepts, as they are required.

Second harmonic generation (SHG) is essentially dictated by symmetry. Actually, SHG is even forbidden (in the dipolar approximation) in centrosymmetric materials, which is rather unfortunate since plasmonic metals such as gold or silver are centrosymmetric [1]. This fact can be easily understood by studying the response of a centrosymmetric crystal using two different arguments: the first one based on the nonlinear susceptibility $\chi^{(2)}$ that provides the second harmonic polarizability $P(2\omega)$, which is at the origin of the SHG signal:

$$P(2\omega) = \chi^{(2)}\, E(\omega)\, E(\omega)\,, \tag{1}$$

where $E(\omega)$ is the excitation field at the fundamental frequency. The second argument is based on the symmetry of the system and appears to contradict the first argument, such that the only possibility is a vanishing second harmonic field.

However, the crystal centrosymmetry is broken at the surface of any structure; thus SHG can occur at the surface of a plasmonic metal. Furthermore, since the plasmon resonances produce strong field enhancement exactly at the surface of the metal, SHG can be significantly enhanced in plasmonic nanostructures, especially in electromagnetic hot spots in the gap between two neighbouring nanostructures. This leads to extremely interesting effects that strongly depend on the surface, the orientation of the nanostructures or their arrangement in a collection of entities [2].

Equation (1) can comprehend quite complicated physics since $\chi^{(2)}$ is in general a tensor and can combine all sorts of different electric field components to produce the nonlinear response. It turns out that for plasmonic metals, it is the components normal to the surface that dominate SHG [1]. This can be implemented in full–wave electromagnetic calculations to obtain both the second harmonic near– and far–fields for plasmonic structures with arbitrary shape. This theoretical understanding is very important for guiding the development of experiments, especially optimizing the shape of plasmonic nanostructures to enhance SHG. I will show that surprising effects associated to the interplay between different components of a multipart plasmonic nanostructure can control the nonlinear signal in a rather complex manner [3].

Another way to look at this optimization of the nonlinear response of plasmonic nanostructures is to consider the optical modes that are supported by the system. Indeed, again because of the symmetries associated with SHG, specific optical modes – like the electric quadrupole – are playing an especially important role in the enhancement of the nonlinear response. Hence, when these specific modes exist either at the fundamental frequency ω or at the second harmonic 2ω, the SHG can significantly enhanced. The coupling between these different modes also influences the dynamics of the nonlinear response [4].

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Spin-photon interface of SiV^- center in nanometer-sized diamond host

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Implementing efficient, highly controllable light-matter interfaces is essential to realizing the goal of solid-state quantum networks. The negatively charged silicon-vacancy (SiV^-) center in diamond is a promising candidate for such interfaces due to favorable optical properties and long coherence times at low temperatures. Creating optical links between remote SiV centers via photon-mediated spin-spin entanglement is an outstanding challenge. An efficient link could be realized by Purcell-enhanced optical transitions by means of optical resonators. The integration of the diamond host into the mode of an optical resonator is demanding and requires, e.g., absence of scattering and optimized coupling. Therefore small dimensions are favorable. However, the resulting proximity of the quantum emitter to the surface of the host matrix typically degrades the optical and coherence properties.

In this talk I will present our work on how to obtain single SiV^- centers per one nanodiamond with ideal optical properties. I will discuss the integration of SiV centers into photonic structures and analyze the achieved coupling efficiency. Furthermore, I will discuss the integration of diamond membranes into fiber-based optical resonators without changing the properties of the cavity. We used the coupled system to extract the absorption cross section of SiV^- centers.

References

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Nano-optics of Surface Plasmon with Electron Beam: Cathodoluminescence Study

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The optical properties of metal nanoparticles (MNPs) that are mainly due to the excitation of localized surface plasmon resonance (LSPR), have been a major focus of research in plasmonics. The LSPR frequency of MNPs can be tuned by varying their size, shape, composition and local dielectric environment [1]. When a MNP sustains LSPR, a strong localized enhancement of the electromagnetic (EM) field amplitude takes place at the MNP surface. The EM field enhancement from such MNPs shows remarkable applications in biosensing and bioimaging, photovoltaics, optical trapping and surface-enhanced Raman scattering (SERS). In this context, the electron beam based spectroscopy techniques, i.e, electron energy loss spectroscopy (EELS) [2] or cathodoluminescence (CL) [3] are excellent alternative probes for LSPs of nanoparticles at single particle level with high spatial resolution. Moreover, in recent years, the time-resolved spectroscopy approach using the electron microscopy [4] has also drawn much attention to understand the mechanisms of charge and energy transfer dynamics in macromolecules and chemical reaction, to name only a few. In this talk, I will discuss about probing the LSPs of metal nanoparticles at single particle level using the electron-beam based spectroscopy. Additionally, I would like to discuss about our recent works to investigate correlations between different photonic systems, using electron microscopes based on the spectral interferometry methodology [5].

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Two-dimensional titanium carbide (MXene) as surface-enhanced Raman scattering substrate

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The implementation of SERS is limited by the cost of SERS substrates (use of noble metals and expensive manufacturing), reproducibility and/or deposition of SERS particles exhibiting inhomogeneity on the substrate. New family of 2D materials - transition metal carbides and nitrides (MXenes) display advantageous properties such as easy synthesis, metallic conductivity, hydrophilicity and flexibility. The most common MXenes Ti_3C_2Tx and Ti_2NTx, where Tx represents the surface terminations (-OH, -F, -O), has already demonstrated promise in biosensing and other applications. We have shown that Ti_3C_2Tx as a support for noble metal nanoparticles for their use in SERS is realizable [1]. After discovering of TiC, TiN and other conductive bulk ceramics possessing plasmonic properties and strong interband absorption, the problem of study of SERS in these materials became important. A method of producing Ti_3C_2Tx SERS substrates with design-inherent hot-spots, yielding SERS enhancement factor (EF) on the order of $10^5 - 10^6$ as well as chemical selectivity to dye molecules was developed in [2]. An optimal percentage of surface coverage by performing a systematic study on a common dye, Rhodamine 6G (R6G) was found. In Fig. 1 (a) the calculated absorption spectra of $MXene_x$ are presented and interband absorption in visible range is manifested. Longitudinal SP absorption takes place at far IR region. Measured UV-vis absorption spectra of Ti_3C_2Tx in aqueous solution with different concentration is presented in the Fig. 1 (b) and a good agreement with experiment is evident.

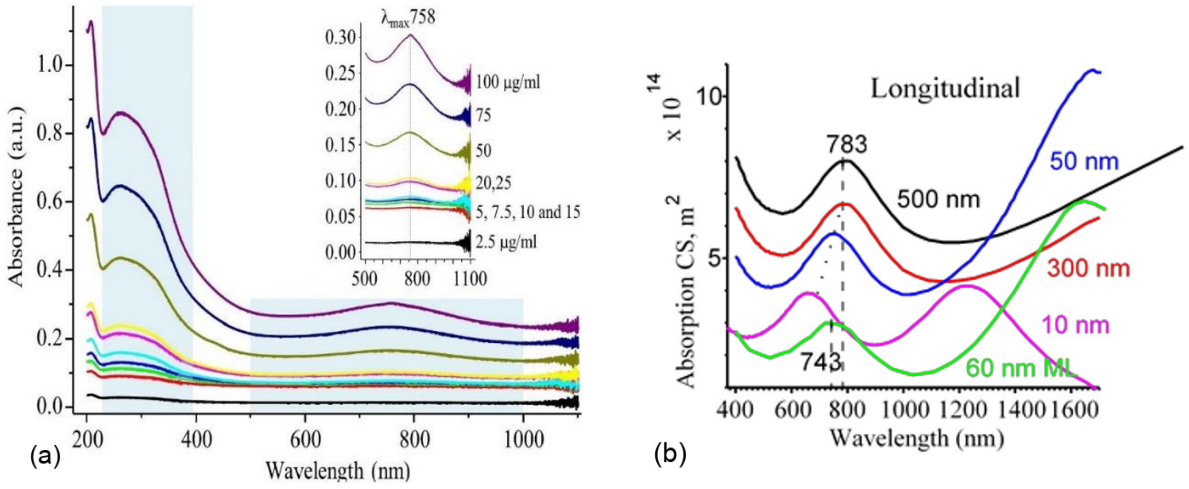

Figure 1: (a) Measured absorption spectra of MXene in aqueous solution with different concentrations. (b) Calculated absorption spectra of MXene spheroids of different aspect ratios.

The measurements of Raman spectra of Ti_3C_2Tx flakes and R6G on Ti_3C_2Tx flakes in water at different pump wavelengths are presented in Fig. 2.

In Fig. 2 (a) the Raman peaks at 200 and 723 cm^{-1} are correspondingly attributed to the Ti-C and C-C vibrations (A_{1g} symmetry) of the oxygen-terminated $Ti_3C_2O_2$. The peak at 620 cm^{-1} comes mostly from E_g vibrations of the C atoms in the OH-terminated MXene. The peaks at 389 and 580 cm^{-1} are attributed to the O atoms E_g and A_{1g} vibrations, respectively. The 282 and 519 cm^{-1} (the latter is enhanced when using a 788 nm excitation) are occurring due to the contribution of H atoms in the OH groups of Ti_3C_2Tx . In Fig. 2 (b) the enhancement factors of experimental data on SERS of R6G on Ti_3C_2Tx flakes for different laser wavelengths are shown. As it can be seen in our experimental situation the EF are $\sim 1.2 \times 10^6$ and 5.3×10^5, for the 514 nm and 488 nm lasers, respectively. In a recent experiment however, the Raman EF of 10^{12} for other MXene - Ti_2N as a substrate was demonstrated using rhodamine 6G with 532 nm excitation wavelength [4]. In order to clarify the possibility of reaching such high value of EF we modeled the flakes as two closely located nanoellipsoids directed along

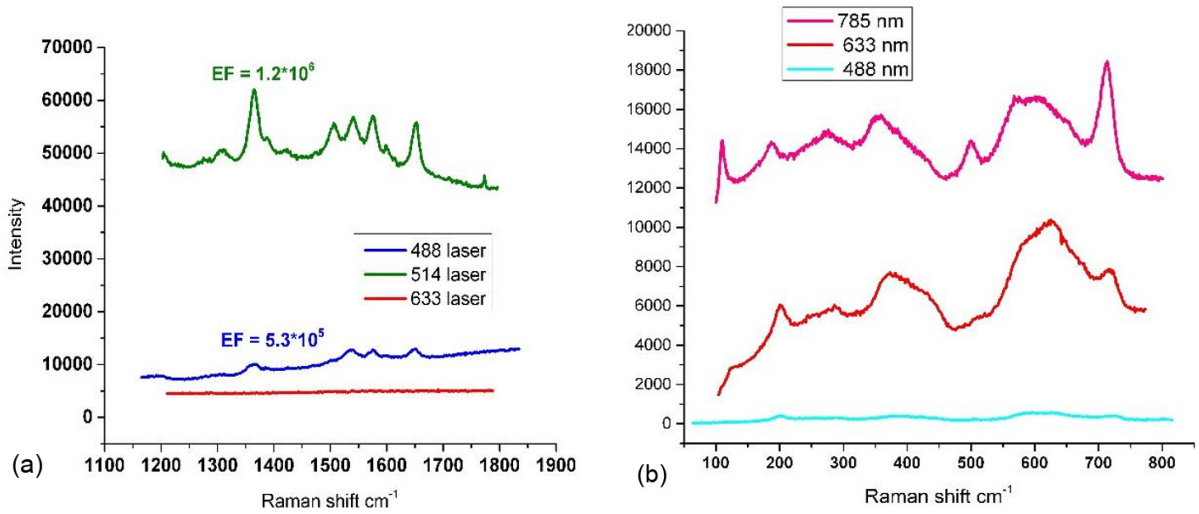

Figure 2: Raman spectra of (a) MXene at different pump wavelengths, and (b) R6G on Ti_3C_2Tx flakes.

their longer axis and dye molecule in the middle. Applying COMSOL software to calculated the electric field at different distances between the nanoellipsoids and dye molecules modeled as point dipole we obtained the EF. Although the measured dielectric functions of MXenes do not provide high EF because of low charge carrier density and broad interband absorption lines, nevertheless special geometry with very sharp edges of flakes less than 1 nm (contrary to noble metal nanoparticles) can provide desirable enhancement.

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