

## CPP 16: Plasmonics and Nanooptics I: Local Probes and Raman (joint session O/CPP)

Time: Monday 10:30–13:45

Location: WIL A317

CPP 16.1 Mon 10:30 WIL A317

**Light emission from charged Hydrogen-Phthalocyanine molecules on NaCl layers** — ●VIBHUTI RAI<sup>1</sup>, LUKAS GERHARD<sup>1</sup>, SUN QING<sup>1</sup>, and WULF WULFHEKEL<sup>1,2</sup> — <sup>1</sup>Institut für Nanotechnologie, Karlsruher Institut für Technologie, 76344 Eggenstein-Leopoldshafen, Germany — <sup>2</sup>Physikalisches Institut, Karlsruher Institut für Technologie, 76131 Karlsruhe, Germany

Recently, light emission studies from single molecules on insulating layers studied by scanning tunneling microscopy (STM) has had made considerable progress. However, many fundamental aspects of light emission remain unclear. In this report, we used a home build STM[1] with high light collection efficiency to investigate the light emission from single Hydrogen-Phthalocyanine ( $H_2Pc$ ) molecules thermally evaporated onto bi- and trilayers of NaCl on Au(111) surface. For the first time we have observed light emission from both charged and neutral  $H_2Pc$  molecules and mapped the spatial dependence of light emission. We find that the photon yield of the charged species is significantly higher than the neutral one and that the tautomerization of the charged  $H_2Pc$  molecule is reflected in the energy and spatial distribution of the emitted light. For further understanding of the fundamental processes of light emission we performed detailed current and voltage dependence of light emission spectra from charged  $H_2Pc$  molecule.

1. Edelmann et al., Review of Scientific Instruments 89, 123107 (2018).

CPP 16.2 Mon 10:45 WIL A317

**Anti-Stokes Light Scattering in an Electrically Biased Plasmonic Nanojunction** — ●SHUYI LIU<sup>1</sup>, MARTIN WOLF<sup>1</sup>, and TAKASHI KUMAGAI<sup>1,2</sup> — <sup>1</sup>Department of Physical Chemistry, Fritz-Haber Institute of the Max-Planck Society, Faradayweg 4-6, 14195 Berlin, Germany. — <sup>2</sup>JST-PRESTO, 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan.

Photon scattering and emission from plasmonic nanostructures have attracted increasing attention but the underlying mechanisms have been debated. [1,2] We report on light scattering from an electrically-biased plasmonic nanocavity, which composed of a Ag tip and Ag(111) surface, using a low-temperature scanning tunneling microscope (STM). It is found that anti-Stokes shifted scattered light is observed occurs when a bias voltage ( $< 2V$ ) is applied to the junction. By observing the scattering spectra in dependence on the spectral shape of the localized surface plasmon resonance (LSPR) in the STM junction, we revealed that either electronic Raman scattering (ERS) or photoluminescence (PL) dominates the process depending on spectral matching of the LSPR with excitation wavelength. We discuss the possibility that ERS occurs by the interaction of the LSPR with a "gap exciton" in the STM junction. Reference: [1] Mertens et al, Nano Lett. 17, 2568-2574 (2017).[2] Cai et al, Anti-Stokes Emission from Hot Carriers in Gold Nanorods. Nano Lett. 19, 1067-1073 (2019).

CPP 16.3 Mon 11:00 WIL A317

**Broadband measurement of local density of optical states by plasmonic nanofocusing spectral interferometry** — ●ABBAS CHIMEH<sup>1</sup>, MARTIN ESMANN<sup>2</sup>, ANKE KORTE<sup>1</sup>, JINHUI ZHONG<sup>1</sup>, NAHID TALEBI<sup>3</sup>, and CHRISTOPH LIENAU<sup>1</sup> — <sup>1</sup>Universität Oldenburg, Oldenburg, Germany — <sup>2</sup>Centre de Nanosciences et de Nanotechnologies, Paris, — <sup>3</sup>Universität Kiel, Kiel, Germany

The local density of optical states (LDOS) is one of the most fundamental quantities in nanophotonics [1]. Experimental mapping of the LDOS enables to understand how a quantum emitter is coupled to its nanostructured photonic environment. Here, we demonstrate a novel experimental approach to directly measure the LDOS with  $< 10$  nm spatial resolution in a broad spectral range. Surface plasmon polaritons (SPPs) propagating along a conical gold taper are adiabatically converted to a local dipole mode at the very apex [2], which can locally excite and detect the optical states around single gold nanoparticles. Integration of an inline interferometer in this plasmonic nanofocusing taper allows us to extract amplitude a phase of local light scattering spectra of gold nanoparticles and quantify line broadenings and spectral shifts induced by tip-sample coupling [3]. We show that, in the limit of weak tip-sample coupling, these measurements directly probe the projected local density of optical states of the plasmonic system.

[1] R. Carminati et al., Surf. Sci. Rep. 70, 1 (2015) [2] M. Es-

mann et al., Nature Nanotechnol. 6, 6040 (2019) [3] M. Esmann et al., Nanophotonics, in press (2020)

CPP 16.4 Mon 11:15 WIL A317

**Spatial and spectral mode mapping of a  $Sb_2S_3$  nanodot by broadband interferometric homodyne scanning near-field spectroscopy** — JINXIN ZHAN<sup>1</sup>, WEI WANG<sup>2</sup>, JENS BRAUER<sup>1</sup>, LUKAS SCHMIDT-MENDE<sup>2</sup>, CHRISTOPH LIENAU<sup>1</sup>, and ●PETRA GROSS<sup>1</sup> — <sup>1</sup>Carl von Ossietzky Universität, Oldenburg, Germany — <sup>2</sup>University of Konstanz, Konstanz, Germany

We present and demonstrate a novel approach towards broadband scattering-type near-field scanning optical spectroscopy based on homodyne mixing and on rapid acquisition of spectra facilitating tip-modulated spectroscopy. We aim at a fast and spectrally resolved near-field measurement of plasmonic and dielectric nanostructures. The weak, broad-bandwidth near field is amplified above the background by homodyne mixing using a Michelson interferometer, and spectral interferograms over a  $> 150$  nm bandwidth are recorded. For rapid acquisition of complete spectra, we use a monochromator and a line camera with 210-kHz readout rate. The near-field spectra obtained after demodulation show supreme background suppression.

We apply this new method to the characterization of  $Sb_2S_3$  semiconductor nanodots fabricated by electron beam lithography.  $Sb_2S_3$  recently became attractive as photovoltaic material, and patterning the surface of a thin film with nanodots of the same material is a strategy to achieve light trapping. Here, we present spatially and spectrally resolved measurements of waveguide-like modes that are excited by below-bandgap illumination. These constitute a practical mechanism for improved below-bandgap absorption in  $Sb_2S_3$  thin film solar cells.

CPP 16.5 Mon 11:30 WIL A317

**Polarization-sensitive near-field optical nanoscopy for investigating optical phonon anisotropies at mid-infrared to THz wavelengths** — ●LUKAS WEHMEIER<sup>1</sup>, TOBIAS NÖRENBERG<sup>1</sup>, THALES V. A. G. DE OLIVEIRA<sup>1,2</sup>, J. MICHAEL KLOPF<sup>2</sup>, SUSANNE C. KEHR<sup>1</sup>, and LUKAS M. ENG<sup>1,3</sup> — <sup>1</sup>Technische Universität Dresden, Germany — <sup>2</sup>Helmholtz-Zentrum Dresden-Rossendorf (HZDR), Germany — <sup>3</sup>ct.qmat, Dresden-Würzburg Cluster of Excellence - EXC 2147, Technische Universität Dresden, Germany

Polarization-sensitive techniques, such as ellipsometry, are of essential value when investigating optically anisotropic (low-dimensional) materials. Yet, polarization is often neglected in scattering scanning near-field optical microscopy (s-SNOM) and spectroscopy. In a first attempt towards quantitative nano-ellipsometry, we demonstrate here the phonon-enhanced resonant near-field excitation when using both p- and s-polarized incident photons. Notably, we find their near-field responses to be on the same order of magnitude [1]. We apply this s-SNOM mimic for inspecting a broad set of crystalline perovskite materials, i.e.  $BiFeO_3$ ,  $PbZrTiO_3$ ,  $SrTiO_3$ , and  $LiNbO_3$ . Their phonon resonances are easily excited by our setup, making use here of the broad tunability range of the free-electron laser FELBE at Dresden-Rossendorf, Germany [1,2]. Hence, we are able to resonantly excite specific phonons, i.e. a single type of vibronic bonding within the crystal in our s-SNOM setup [2].

[1] L. Wehmeier et al., Phys. Rev. B 100, 035444 (2019).

[2] L. Wehmeier et al., Appl. Phys. Lett., submitted (2019).

CPP 16.6 Mon 11:45 WIL A317

**Single-molecule vibrational signature and redox-states probed with STM-Induced Fluorescence Microscopy** — ●BENJAMIN DOPPAGNE, MICHAEL C. CHONG, ETIENNE LORCHAT, STEPHANE BERCIAUD, MICHELANGELO ROMEO, HERVÉ BULOUE, ALEX BOEGLIN, FABRICE SCHEURER, and GUILLAUME SCHULL — Institut de Physique et Chimie des Matériaux de Strasbourg, 67034 Strasbourg, France

Infrared, Raman and fluorescence spectroscopies are powerful methods to obtain precise information regarding the chemical structure or environment of an organic system. In this presentation, I report the use of a STM to obtain the fluorescence spectrum of a single Zinc-Phthalocyanine molecule, to go beyond the limitations commonly observed in conventional optical techniques. We have shown that in such configuration, it is possible to obtain optically an accurate vi-

brational signature of the probed molecule with a sub-molecular resolution, without light excitation. This technique has allowed us to obtain, for the first time, the fluorescence spectrum of a charged single molecule. Comparison between fluorescence spectra of the neutral and the charged species shows that these latter exhibit different vibrational signatures. Thanks to this identification, we performed a complete optical monitoring of the redox state of a single molecule with STM-Induced Fluorescence Microscopy.

CPP 16.7 Mon 12:00 WIL A317

**Optical tracking of a tautomerization process with STM-Induced Fluorescence Microscopy** — ●BENJAMIN DOPPAGNE<sup>1</sup>, TOMAS NEUMAN<sup>2</sup>, RUBEN SORIA MARTINEZ<sup>1</sup>, LUIS E. PARRA LOPEZ<sup>1</sup>, HERVÉ BULOUE<sup>1</sup>, MICHELANGELO ROMEO<sup>1</sup>, STEPHANE BERCLAUD<sup>1</sup>, FABRICE SCHEURER<sup>1</sup>, JAVIER AIZPURUA<sup>2</sup>, and GUILLAUME SCHULL<sup>1</sup> — <sup>1</sup>Institut de Physique et Chimie des Matériaux de Strasbourg, 67034 Strasbourg, France — <sup>2</sup>Center for Materials Physics, San Sebastian 20018, Spain

Optical spectroscopies are powerful techniques to obtain precise information regarding the chemical structure or the environment of organic molecules. Therefore, gathering the optical signal from a single molecule represents the ultimate limit in terms of chemical analysis and provide a way to probe its local environment. In this presentation, I report recent results, where we used a STM to induce fluorescence emission from a single H2Pc molecule. Two different emission lines, which are relative to each tautomer of the molecule are observed in the STM-Induced fluorescence spectrum. Spatial mapping of these fluorescence lines coupled with a theoretical model using the concept of plasmonic picocavity, where the light is confined by the last atoms of the tip within volumes of the order of 1 nm<sup>3</sup>, allowed us to obtain optical images of the two tautomers. Thanks to this identification, real-time optical tracking of the tautomerization process is carried out, providing the tautomers lifetimes. This result shows that STM-Induced single-molecule fluorescence experiments constitute a complete optical microscopy technique at the atomic scale.

CPP 16.8 Mon 12:15 WIL A317

**Compensating for electrostatically-induced artifacts in scanning near-field optical microscopy** — ●TOBIAS NÖRENBERG<sup>1</sup>, SUSANNE C. KEHR<sup>1</sup>, and LUKAS M. ENG<sup>1,2</sup> — <sup>1</sup>Institute of Applied Physics, Technische Universität Dresden, Germany — <sup>2</sup>ct.qmat: Dresden-Würzburg Cluster of Excellence - EXC 2147, Technische Universität Dresden, Germany

Nanotechnology and modern material sciences demand reliable local probing techniques with nanometer resolution. In particular, scattering-type scanning near-field optical microscopy (s-SNOM) is a well-established method that is sensitive to the local optical response of a sample, yielding a wavelength-independent lateral resolution on the order of ~10 nm. Nevertheless, local variations of the electric potential at the sample surface may dramatically affect the tip-sample interaction, thereby introducing artifacts in both optical near-field signal and topography.

Here, we present a comprehensive experimental study investigating the mentioned artifacts for different sample systems, i.e. metals (Au), semiconductors (Si), and insulators (SiO<sub>2</sub>). By combining s-SNOM with Kelvin-probe force microscopy (KPFM) we firstly fully compensate for these errors, while secondly also being able to measure such local potentials. Optical, topographic, and electronic information hence become well separated and quantified.

CPP 16.9 Mon 12:30 WIL A317

**Tip-Enhanced Raman Scattering of CdSe-CdS Nanoplatelets on Plasmonic Substrates** — ●ILYA MILEKHIN<sup>1</sup>, MAHFUJUR RAHAMAN<sup>1</sup>, TATYANA DUDA<sup>2,3</sup>, EKATERINA RODYAKINA<sup>2,3</sup>, KIRILL ANIKIN<sup>2,3</sup>, ROMAN VASILIEV<sup>4</sup>, VOLODYMYR DZHAGAN<sup>5</sup>, ALEXANDER MILEKHIN<sup>2,3</sup>, ALEXANDER LATYSHEV<sup>2,3</sup>, and DIETRICH RT ZAHN<sup>1</sup> — <sup>1</sup>Semiconductor Physics, Chemnitz University of Technology, Chemnitz, Germany — <sup>2</sup>A.V. Rzhanov Institute of Semiconductor Physics RAS, Novosibirsk, Russia — <sup>3</sup>Novosibirsk State University, Novosibirsk, Russia — <sup>4</sup>Department of Material Science, Moscow State University, Moscow, Russia — <sup>5</sup>V.E. Lashkaryov Institute of Semiconductor Physics, Kiev, Ukraine

We present the results on a gap-plasmon tip-enhanced Raman scattering (TERS) study of core-shell CdSe-CdS nanoplatelets (NPs) deposited on periodic arrays of Au nanodisks which serve as plasmonic substrates. The fabrication of Au nanodisks with a diameter of 110 nm and a height of 50 nm on Si substrates covered with a 77 nm of SiO<sub>2</sub>

was performed by electron beam lithography. NPs with a characteristic size of 100x30x3 nm were deposited onto the plasmonic substrate using the Langmuir-Blodgett technique. We observe a remarkable Raman enhancement of the phonon modes of CdSe and CdS from NPs located in the plasmonic gap between Au nanodisks and TERS tip. Gap-mode TERS imaging was performed at 638 and 785 nm excitation and allowed us to visualize the near field distribution of the gap-plasmon with relative TERS contrast of 30. A phonon response of the single NP was achieved with a spatial resolution of 2 nm.

CPP 16.10 Mon 12:45 WIL A317

**The influence of size and shape of tip and substrate in gap-mode tip-enhanced Raman spectroscopy** — ●LU HE, MAHFUJUR RAHAMAN, TERESA I. MADEIRA, and D.R.T. ZAHN — Semiconductor physics, University of technology Chemnitz, Germany

Tip-enhanced Raman Spectroscopy (TERS) utilizes the confined electric field in the vicinity of a metal tip. The typical spatial resolution is around 2 nm[1] and even sub-nanometer can be achieved[2,3]. Many factors play a role in the TERS technique[4]. Our simulation focuses on the comparison of the two configurations. The first one consists of various tip radii with thin film while the second one consists of a constant tip radius with various radii of spherical substrates in a metal-metallic gap-mode TERS system using the finite element method (FEM). An unusual shift in the first case is observed. An improved expression of the above approximation is obtained for the second case.

CPP 16.11 Mon 13:00 WIL A317

**Probing the Local Generation and Diffusion of Active Oxygen Species on a Pd/Au Bimetallic Surface by Tip-Enhanced Raman Spectroscopy** — HAI-SHENG SU<sup>1</sup>, ●JIN-HUI ZHONG<sup>2,1</sup>, and BIN REN<sup>1</sup> — <sup>1</sup>State Key Laboratory of Physical Chemistry of Solid Surfaces, iChEM, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China. — <sup>2</sup>Institute of Physics, Carl von Ossietzky University, Oldenburg 26129, Germany

In this contribution, we discuss the application of tip-enhanced Raman spectroscopy (TERS) to image local atomic site-specific electronic and catalytic properties of bimetallic Pd monolayer/Au(111) [1] and Pt nanoisland/Au(111) surface [2]. The high spatial resolution (<3 nm) of TERS allows us to reveal distinct properties of surface atoms that correlate to the catalytic properties. We further probe the local generation and diffusion of OH radicals on a Pd monolayer/Au(111) bimetallic catalyst surface [3]. The reactive OH radicals can be catalytically generated from hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) at the active Pd step edge site and could diffuse to both the Au and Pd surface sites to induce oxidative reactions, with a diffusion length estimated to be about 5.4 nm. The results suggest the capability of TERS, as a plasmon-enhanced nanoscopy, to in-situ study catalysis with unprecedented spatial resolution and rich molecular identity. [1] J.-H. Zhong, B. Ren\*, et al., Nat. Nanotech., 2017, 12, 132. [2] H.-S. Su, J.-H. Zhong\*, B. Ren\*, et al., Angew. Chem. Int. Ed. 2018, 57, 13177. [3] H.-S. Su, J.-H. Zhong\*, B. Ren\*, et al., submitted.

CPP 16.12 Mon 13:15 WIL A317

**Strong surface plasmon localization in gold nanosponges probed by plasmonic nanofocusing spectroscopy** — ●ANKE KORTE<sup>1</sup>, ABBAS CHIMEH<sup>1</sup>, JINHUI ZHONG<sup>1</sup>, DONG WANG<sup>2</sup>, PETER SCHAAP<sup>2</sup>, and CHRISTOPH LIENAU<sup>1</sup> — <sup>1</sup>Carl von Ossietzky Universität Oldenburg, Germany — <sup>2</sup>Technische Universität Ilmenau, Germany

Porous gold nanosponges, percolated with a three-dimensional network of 10 nm sized ligaments, recently emerged as promising substrates for plasmon-enhanced spectroscopy. Experimental and theoretical studies suggest surface plasmon localization in small hot-spots. To probe the existence of such hot-spots, we have first used scattering-type scanning near-field optical microscopy with homodyne detection of the scattered signal from individual nanosponges to reveal such strong spatially and spectrally confined modes. By recording local near-field scattering spectra, high quality factors of 40 for individual hot-spots are demonstrated. More recently, we combined this method with plasmonic nanofocusing, where surface plasmon polaritons propagate along the shaft of a conical gold taper and form an isolated nano light source. This removes unwanted background since hot-spot modes are locally excited just by the nano-localized tip dipole field, resulting in a highly improved signal-to-noise-ratio and a simplified image interpretation. This advanced technique is used to investigate the coupling behaviour between such hot-spot modes and small quantum emitters, which were deposited inside the pores of a nanosponge.

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**Resonant, plasmonic enhancement of alpha-6T molecules encapsulated in CNTs** — •SÖREN WASSERROTH<sup>1</sup>, SEBASTIAN HEEG<sup>1,2</sup>, NICLAS MUELLER<sup>1</sup>, PATRYK KUSCH<sup>1</sup>, UWE HÜBNER<sup>3</sup>, ETIENNE GAUFRÈS<sup>4</sup>, NATHALIE TANG<sup>4</sup>, RICHARD MARTELL<sup>4</sup>, ARAVIND VIJAYARAGHAVAN<sup>2</sup>, and STEPHANIE REICH<sup>1</sup> — <sup>1</sup>Freie Universität Berlin, Berlin, Germany — <sup>2</sup>The University of Manchester, Manchester, UK — <sup>3</sup>Leibniz IPHT, Jena, Germany — <sup>4</sup>Université de Montréal, Montréal, Canada

Surface-enhanced and resonant Raman scattering are widely used techniques to enhance the Raman intensity by several orders of magnitude. SERS uses plasmonic near-fields to enhance the Raman scattering process, whereas electronic transitions are the origin of the enhancement

in resonant Raman scattering. Typical Raman reporters in SERS are molecules; in SERS experiments, the intrinsic resonance of the molecules is often ignored. We present a wavelength dependent Raman study of sexithiophenes encapsulated in carbon nanotubes. To distinguish between the intrinsic resonance and plasmonic enhancement we investigate different tube bundles with and without plasmonic near field. The filled nanotubes are placed precisely in a gold dimer gap by dielectrophoretic deposition. Polarization dependent Raman measurements confirmed the alignment of the molecules within the nanotubes and the influence of the plasmonic near-field. By tuning the excitation wavelength, we were able to determine the intrinsic molecular resonance and observed a strong redshift towards the plasmon resonance of maximum Raman intensity under plasmonic enhancement.