

CPP 32: Focus Session: Novel Approaches to Surface Plasmon Generated Charges and Heat for Photocatalysis I (joint session O/CPP)

Plasmonic nanostructures present efficient optical antennas to generate energetic charges and/or localized heat for the use in photocatalysis. The time and length scales of typical plasmon-induced processes however pose a formidable challenge, which today still hinders the large-scale implementation of plasmon photocatalysis. The aim of this focus session is to discuss the physical mechanism of plasmon-induced charge-transfer and heat generation processes and exchange ideas on novel materials and devices utilizing these processes.

Organizers: Marc Herzog, Wouter Koopman (U Potsdam)

Time: Wednesday 15:00–17:30

Location: MA 141

Topical Talk

CPP 32.1 Wed 15:00 MA 141

Plasmonic photothermal chemistry on single nanoparticles — ●ANDREA BALDI — Vrije Universiteit Amsterdam, The Netherlands

Metal nanoparticles strongly absorb light thanks to light-driven oscillations of their free electrons called plasmon resonances. The decay of these resonances can be used to drive chemical reactions via heating of the surrounding environment. In this talk, I will show how we quantify photothermal heating on single nanoparticles using a novel Raman-based thermometry [1] and how we use localized temperature gradients to drive the synthesis of hierarchical core-shell nanostructures [2].

[1] P. Li, S. H. C. Askes, E. del Pino Rosendo, F. Ariese, C. Ramanan, E. von Hauff, and A. Baldi, *Nanoscale Thermometry of Plasmonic Structures via Raman Shifts in Copper Phthalocyanine*, *J. Phys. Chem. C* 2023, 127, 9690-9698

[2] R. Kamarudheen, G. Kumari, and A. Baldi, *Plasmon-driven synthesis of individual metal@semiconductor core@shell nanoparticles*, *Nature Communications* 2020, 11:3957

CPP 32.2 Wed 15:30 MA 141

Single molecule layer temperature control via electrically connected SERS gratings — ●THORSTEN FEICHTNER¹, POOJA SUTHEESHANAN², PAUL MÖRK¹, ENNO SCHATZ³, and BERT HECHT¹ — ¹Nano- Optics & Biophotonics Group, Department of Experimental Physics 5, Röntgen Research Center for Complex Material Research (RCCM), Physics Institute, University of Würzburg, Am Hubland, D-97074 Würzburg, Germany — ²School of Physics, IISER Thiruvananthapuram, India — ³NanoStruct GmbH, Friedrich-Bergius-Ring 15, 97076, Würzburg

It would be beneficial for photoelectrochemical experiments in microfluidic environments to be able to locally heat and directly measure the realized temperature. Surface enhanced Raman scattering can be used to locally measure the temperature of molecules, as the scattering peak heights depend on the probability density of vibrational states.

Here we provide evidence that our recently developed two wire grating SERS substrates [1] can be heated very locally using its Ohmic resistance. We measure its resulting temperature using the Raman peaks of a self-assembled monolayer of 4-MBA molecules in dependency of the heating current and fitting a probability density function approach. We back up the experiment with optical and heat simulations. This platform is ready to be implemented in microfluidic systems to measure SERS at the very same position where heat is applied.

[1] Sweedan, Amro, et al., arXiv preprint arXiv:2308.01395 (2023).

CPP 32.3 Wed 15:45 MA 141

Superlattice excitation driven by electron-phonon interaction measured with UXR — ●JAN-ETIENNE PUDELL¹, MARC HERZOG², MAX MATTERN², ALEXANDER VON REPPERT², DANIEL SCHICK³, ULRIKE BOESENBERG¹, ANGEL RODRIGUEZ-FERNANDEZ¹, WONHYUK JO¹, ROMAN SHAYDUK¹, WEI LU¹, GREGORY MALINOWSKI⁵, MICHEL HEHN⁵, MATIAS BARGHEER^{2,4}, and ANDERS MADSEN¹ — ¹European XFEL, Germany — ²Institut für Physik, Uni Potsdam, Germany — ³MBI, Berlin — ⁴HZB Berlin, Germany — ⁵IJL, Université Lorraine, France

The transport of heat (or energy in general) in nanoscopic heterostructures is of great fundamental as well as technological interest, e.g. in the context of thermal management in devices, heat-assisted magnetic recording or plasmonic catalysis. In metal heterostructures, heat conduction is usually dominated by electrons which can be at strong non-equilibrium with lattice vibrations on ultrashort time scales. Utilizing ultrafast x-ray diffraction (UXRD) at the MID end-station at

European XFEL, we investigate the ultrafast structural response of a laser-excited metal-metal superlattice (SL) consisting of few-nm thick metal layers with low (Cu) and high (Pt) electron-phonon coupling on top of a 100 nm Cu and 20 nm Ni layer. Using the transient shift and intensity modulations of the respective Bragg peaks, we can quantify the ultrafast heat flow in the SL by comparison to a time-dependent diffusive two-temperature transport model. We identify the excitation of the SL phonon mode as well as an efficient heat transport from the laser excited SL to the Ni-layer via hot electrons.

CPP 32.4 Wed 16:00 MA 141

How to evaluate temperature at single-molecule, single-particle and ensemble levels — ●SIMONE EZENDAM, JULIAN GARGIULO, and EMILIANO CORTÉS — Physics department, University of Munich, Germany

Understanding temperature dynamics across various scales (single-molecule, single-particle, and ensemble) is pivotal in harnessing plasmonic catalysis for enhanced chemical reactivity. We present three studies investigating this intricate interplay. First, employing super-resolution fluorescence microscopy, we probe single-particle plasmonic catalysis, unveiling distinct pathways and spatial reactivity [1]. Second, through single-particle thermometry, we explore morphology-driven light-to-heat conversion in Au/Pd nanoparticles, unraveling intriguing photothermal responses [2]. Finally, we introduce Anti Stokes thermometry to measure temperature in plasmonic ensembles, validating its efficacy in understanding light-induced heating of nanoparticle arrays [3]. These findings deepen our understanding of plasmonic heating, guiding the design of future nanocatalysts.

[1] 10.1021/acsnano.3c07833, [2] 10.1038/s41467-023-38982-9 [3] 10.1002/adom.202301496

CPP 32.5 Wed 16:15 MA 141

Measurement of temperature gradients at plasmonic metal surface using thermosensitive microgels — ●YULIA GORDIEVSKAYA¹, NINO LOMADZE¹, SE-HYEONG JUNG², ANDRIJ PICH^{2,3}, and SVETLANA SANTER¹ — ¹University of Potsdam, Potsdam, Germany — ²RWTH Aachen University, Aachen, Germany — ³Aachen Maastricht Institute for Biobased Materials (AMIBM), Geleen, The Netherlands

Microgels are recognized for their remarkable responsiveness to changes in environmental conditions[1]. Here, we presented a novel method for local temperature determination in aqueous solutions by observing the inhomogeneous collapse of microgels positioned at plasmonic metal surface. The surface is a variable-thickness gold layer(5-30nm) deposited on glass coated with titanium oxide(<1nm). The localized laser irradiation of the substrate results in the absorption of light by the gold layer, converting it into heat [2]. We studied how the laser wavelength and power levels, as well as distance from the irradiation spot influence the size and shape of the thermosensitive PNIPAM microgel. The obtained dependences allowed us to construct a comprehensive temperature distribution profile relative to the irradiation point.

We thank SFB 1636: Elementary processes of light driven reactions at the nanoscale. [1] J. Jelken, S.-H. Jung, N. Lomadze, Yu.D. Gordievskaya, E.Yu. Kramarenko, A. Pich, S. Santer. *Advanced Functional Materials* 32.2 (2022), p. 2107946. [2] V. Muraveva, M. Bekir, N. Lomadze, R. Großmann, C. Beta, S.Santer. *Applied Physics Letters* 120.23 (2022), p. 231905.

Topical Talk

CPP 32.6 Wed 16:30 MA 141

Disentangling plasmonic catalysis contributions by time-resolved spectroscopy — ●HOLGER LANGE — The Hamburg Centre

for Ultrafast Imaging — Institute of Physics and Astronomy, University of Potsdam

According to current understanding, the nanoparticle plasmon decay is a series of sequential scattering events, separated by their timescales of vastly increasing duration. At first, Landau damping polarizes the electron density. Electron-electron scattering equilibrates the excess energy and subsequent electron-phonon coupling leads to rapid electron cooling and a simultaneous increase in lattice temperature. Several of these processes might contribute to the reaction rate enhancement on plasmonic nanoparticles. I will discuss a range of experiments to specifically address the individual steps of the plasmon decay. The temperature of the thermalized hot electron gas can be observed as a contrast in optical pump-probe experiments, the excited lattice is accessible by time-resolved x-ray scattering. I will present the first reconstruction of the decaying gold nanoparticle plasmon field in the time domain by the detection of transient currents. This data combined with reaction dynamics studies under monochromatic excitation reveals both, non-equilibrium carriers and field-induced excitation as most relevant contributions for two different reactions, highlighting the selectivity of the processes.

CPP 32.7 Wed 17:00 MA 141

In situ Observation of Nanoparticle Photocharging: Gold Nanorods as Photochemical Capacitors — ●FELIX STETE¹, WOUTER KOOPMAN¹, and MATIAS BARGHEER^{1,2} — ¹Institut für Physik & Astronomie, Universität Potsdam, Karl-Liebknecht-Str. 24-25, 14476 Potsdam, Germany — ²Helmholtz Zentrum Berlin, Albert-Einstein-Str. 15, 12489 Berlin, Germany

Light can induce charge on plasmonic nanoparticles. This idea was used in the last years to explain experimental results on chemical reactions on gold and silver nanoparticles. Here, we give spectroscopic evidence for this photocharging effect and present a method to examine the charge transfer from a hole scavenger to gold nanorods in situ. In contrast to the plasmon resonance in gold nanospheres, the longitudinal resonance of gold nanorods is very sensitive to the free

electron density in the metal. We show here how the illumination with light blue-shifts the resonance visualizing the transfer of electrons from ethanol in the solution to the nanoparticles and model the intensity-dependence in a capacitor model. The peak can also be shifted back again after illumination when the particles are left in dark or exposed to molecules with a low reduction potential. We discuss how particle size, oxygen in the solution or the absence of ethanol influence the particle charging.

CPP 32.8 Wed 17:15 MA 141

Catalytic Electron Transfer Inhibited by Coulomb Blockade in Au Nanoparticles — ●MONALISA GARAI and THOMAS KLAR — Institute of Applied Physics, Johannes Kepler University Linz, Altenberger Straße 69, 4040 Linz

Colloidal noble metal nanoparticles (NPs) are excellent catalysts for various chemical redox reactions. They offer alternative reaction pathways and thereby significantly reduce the activation energy for chemical transformations. There are several strategies to reduce the activation energy for kinetically sluggish catalytic reactions, e.g. by changing the size, shape and composition of the NPs and also by changing the specific reaction conditions. To investigate the reaction mechanism of Au NPs of different sizes below 10 nm, we used the 1-electron transfer from ferricyanide (Fe^{3+}) to ferrocyanide (Fe^{2+}) as a model reaction system. We compared the reaction rate of the conversion from Fe^{3+} to Fe^{2+} in the presence and absence of the reducing agent triethanolamine (TEOA). It has been shown that the reaction pathway is significantly altered with and without TEOA. TEOA generally transfers electrons to Au NP and causes a negative charging on the Au NP surface. However, if the size of the NPs is very small, especially below 5 nm, the negative charging of the Au NPs is inhibited by the Coulomb blockade effect. As a result, the subsequent catalytic electron transfer from Au NP to Fe^{3+} is also inhibited, which decreases the overall Fe^{3+} reduction rate. These experimental results and theoretical calculations will help to develop novel metal NPs for various catalytic processes for environmental remediation.