

CPP 40: Focus Session: Novel Approaches to Surface Plasmon Generated Charges and Heat for Photocatalysis II (joint session O/CPP)

Time: Thursday 10:30–13:15

Location: MA 141

Topical Talk CPP 40.1 Thu 10:30 MA 141
Designing Plasmonic Photocatalysts — ●EMILIANO CORTES — Nanoinstitute Munich, Faculty of Physics, University of Munich (LMU), Munich, Germany

Nanostructured surfaces and colloids with designed optical functionalities - such as plasmonic & photonic nano and metamaterials - allow efficient harvesting of light at the nanoscale. Exploiting light-driven matter excitations in these artificial materials opens up a new dimension in the conversion and management of energy at the nanoscale [1-4]. One example are plasmonic and photonic catalysts, that can indeed confine solar energy into molecular regions [4-11]. In this talk, I will present our recent efforts in order to understand the light-matter interaction in plasmonic nanoparticles and metamaterials for photocatalysis [1-11].

References [1] E. Cortés, *Nature* 614, 230-232 (2023) [2] E. Cortés, et al. *Nature Rev. Chem.*, 6, 259-274 (2022) [3] E. Cortés, et al. *Chem. Rev.* 122, 15082-76 (2022) [4] S. Ezendam, et al. *ACS Energy Letters*, 7, 778-815 (2022) [5] M. Herran, et al. *Adv. Funct. Mat.*, 2203418 (2022) [6] J. Gargiulo, et al. *Nature Communications* 14, 3813 (2023) [7] L. Nan, et al. *Nano Letters* 23 (7), 2883-2889 (2023) [8] A. Stefancu, et al. *ACS Nano* 17 (3), 3119-3127 (2023) [9] L. Hüttenhofer, et al., *Adv. Energy Mat.*, 46, 2102877 (2021) [10] M. Herran, et al. *Nature Catalysis*, accepted (2023) [11] S. Ezendam, et al. *ACS Nano*, accepted (2023)

CPP 40.2 Thu 11:00 MA 141
Plasmon assisted Catalytic Conversion of CO₂ with Disordered Cu-Pd Network — ●OLIVER WIPF¹, JELENA WOHLWEND¹, DAVID KIWIC², MARKUS NIEDERBERGER², RALPH SPOLENAK¹, and HENNING GALINSKI¹ — ¹Laboratory for Nanometallurgy, ETH Zürich, Switzerland — ²Laboratory for Multifunctional Materials, ETH Zürich, Switzerland

The catalytic conversion of carbon dioxide is currently at the forefront of research as a way to mitigate the climate crisis by capturing CO₂ and turning it into functional chemical components. However, currently this is a high energy consumption process, thus, developing efficient catalysts is critical. Using solar radiation to drive and catalyze chemical reactions could address this challenge. Here, we explore the plasmon assisted catalytic conversion of CO₂ with disordered network metamaterials (DNMs). DNMs are an emerging class of metamaterials with tunable quasi-perfect absorption over a broad range of wavelengths. The optical response of such disordered networks can be conceptualized as coupled dipole-like networks, where the disorder of the metallic network traps and localizes surface plasmon (SP) waves. In this work we harness DNMs as a platform to drive the conversion of CO₂ by taking advantage of "hot" carriers, i.e. electron-hole (e-h) pairs, resulting from the non-radiative decay of plasmons. The generation of hot carriers is dependent on the chemistry and the local geometry, both tailorable with our fabrication route. Furthermore, we show that through chemical engineering of the DNMs, selectivity of the reaction products can be achieved.

CPP 40.3 Thu 11:15 MA 141
Advancing Plasmonic Charge Transfer for Photocatalysis: Bottom-Up Strategies in Energy Harvesting and Optoelectronics — ●SWAGATO SARKAR¹ and TOBIAS A. F. KOENIG^{1,2} — ¹Leibniz-Institut für Polymerforschung Dresden e.V., Hohe Straße 6, 01069 Dresden — ²Center for Advancing Electronics Dresden (cfaed), Technische Universität Dresden, Helmholtzstraße 18, 01069 Dresden

Our study comprehensively explores bottom-up techniques for plasmonic charge transfer, focusing on their collective applications in energy harvesting. Extending the concepts of plasmon-photon hybridization to self-assembled plasmonic nanoparticle chains or deposited metallic nanobars introduces a scalable approach for charge injection to adjacent semiconductor thin films, thus facilitating cost-effective photodetection [Sarkar et al., *Adv. Funct. Mat.*, 2021, 2011099]. The fusion of soft-lithography with template-assisted self-assembly further enhances large-scale bottom-up strategies, providing a cost-efficient printing of plasmonic metasurfaces for superior charge transfer and amplified the photocatalytic processes [Sarkar et al., *Adv. Funct. Mat.*, 2021, 2105054]. Complementing these studies, introducing a novel in-

terconnected metal-semiconductor grating design showcases enhanced current modulation, allowing for efficient photosensor development by leveraging plasmon-mediated hot electrons [Sarkar et al., *Adv. Funct. Mat.*, 2023, 2210172]. Thus, our unified approach to bottom-up techniques in plasmonic charge transfer advances the field and promises efficient and scalable solutions for miniaturized optoelectronic devices.

CPP 40.4 Thu 11:30 MA 141
Electrochemistry at the surface of electrically connected plasmonic resonators — ●PAUL MÖRK¹, AMRO SWEEDAN², MUHAMMAD Y. BASHOUTI², BERT HECHT¹, and THORSTEN FEICHTNER¹ — ¹Nano-Optics & Biophotonics Group, Experimental Physics 5, University of Würzburg, Am Hubland, 97074 Würzburg, Germany — ²Ilse-Katz Institute for Nanoscale Science & Technology, Ben-Gurion University of Negrev, POB 653, Beer-Sheba Campus, Building 51, 8410501, Israel

Electrochemical reactions can be enhanced by catalytic processes at gold surfaces. Nanostructuring can lead to plasmonic resonances in the visible wavelength which may be used for photon routing, local heating or hot electron generation. This way it is possible to tailor the properties of gold for specific photo-electrochemical processes.

Here we discuss the use of electrically connected double-wire gratings as an effective plasmonic platform [1]. The gratings are fabricated from monocrystalline gold platelets via focused ion beam milling. We observe the electrochemical oxidation and reduction of these gold double-wire gratings at ambient conditions when applying voltages up to 10 V over gaps of 20 nm in width. We further show the dimerization of 4-aminothiophenol under continuous irradiation and the reverse reaction in presence of an applied voltage. Finally, we show a first implementation of the gratings as electrodes within nanofluidic channels for future applications as electrochemical cell.

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

CPP 40.5 Thu 11:45 MA 141
Atomic scale plasmonic catalysis — ●YICUI KANG and EMILIANO CORTÉS — Nanoinstitute Munich, LMU Muenchen, Germany

In the realm of plasmonic catalytic systems, much attention has been devoted to the plasmon-derived mechanisms¹, yet the influence of nanoparticles (NPs) crystal facets has been sparsely investigated. In this work², we study the plasmon-assisted electrocatalytic CO₂RR using three different shapes of plasmonic Au nanocube (NC), rhombic dodecahedron (RD) and octahedron (OC) - with different exposed facets: {100}, {110} and {111}, respectively. Upon plasmon excitation, Au OCs and NCs exhibited nearly a doubling in the FE(CO) compared to non-illuminated response. In contrast, RDs showed nearly the same performance in dark or light conditions. Electromagnetic modeling showed higher electric field (EF) enhancement on OCs and NCs on the edges and corners, which in some degree contributes to the enhancement of CO production³. Large-scale atomistic simulations of the electronic structure revealed higher hot carrier abundance on OCs and NCs compared to RDs. Abundant hot carriers on edges facilitate molecular activation, leading to enhanced selectivity and activity. This observation is further supported by plasmon-assisted HER experiments. Our findings highlight the dominance of low coordinated sites over facets in plasmonic catalytic processes, providing valuable insights for designing more efficient catalysts for energy conversion and carbon neutralization. Ref1. *ACS Energy Letters* 7.2 (2022): 778-815 Ref2. *Crystal Facet Effect in Plasmonic Catalysis. Revision* (2023) Ref3. *Angew.Chem.Int.Ed.*61.44 (2022): e202212640

CPP 40.6 Thu 12:00 MA 141
Translucent aerogel supports for photocatalysis — ●DAVID KIWIC, FABIAN MATTER, and MARKUS NIEDERBERGER — Laboratory for Multifunctional Materials, Department of Materials, ETH Zürich, Vladimir-Prelog-Weg 5, 8093 Zürich, Switzerland

Efficient light absorption is a key part of designing a photocatalytic process. In catalysts light can be scattered or absorbed before reaching the intended absorption site. Metal oxide aerogel supports minimize these light transport losses and their open porous structure enables sufficient gas transport to the active sites. These photocatalysts can be fabricated by synthesizing selected metal oxide nanoparticles, co-

gelling them with plasmonic nanoparticles, shaping them into granules via extrusion and subsequent super-critical drying. Pd on ZrO₂ is known in the field of conventional thermal catalysis to be highly active for CO₂ reduction, a key reaction for the decarbonization of our economy. Additionally, Pd nanoparticles strongly absorb visible light and shall be investigated for their photocatalytic activity. Aerogel granules were produced and catalytically tested in thermal and photothermal catalysis with a custom-built reactor setup that enables simultaneous heating and illumination of the granules in the fixed bed. The space time yield of the main product CO was increased manifold by illumination with two white LEDs, demonstrating the great potential of translucent aerogels as support materials for photocatalysis.

CPP 40.7 Thu 12:15 MA 141

Plasmonically generated low-energy electrons: the decomposition of DNA nucleobases derivatives study case — ●SERGIO KOGIKOSKI JUNIOR¹, JANKA KOPYRA², JANUSZ RAK³, and ILKO BALD¹ — ¹Institute of Chemistry, University of Potsdam, Germany — ²Faculty of Sciences, Siedlce University of Natural Sciences and Humanities, Poland — ³Faculty of Chemistry, University of Gdansk, Poland

One outcome of the excitation of plasmonic nanoparticles is the generation of low-energy charge carriers ($E < 0.5$ eV). Our group showed that such charge carriers could drive chemical reactions at the interface of Au and Ag nanoparticles using different probe molecules, such as bromoadenine. However, it is still unclear how such molecule activation happens and what the energy of these carriers is. Herein, we used modified DNA nucleobases as probes to understand the role of the support metal and the low-energy electrons generated. The activation mechanisms to drive reactions using low-energy electrons are already well-studied in the gas phase of such molecules, providing a suitable theoretical background. SERS was used to obtain the molecular fingerprint of the system during irradiation. Our results show that irradiated AgNPs can decompose uracil and adenine derivatives, possibly related to the higher amount and energy of the generated hot electrons. Also, adenines are readily decomposed, even though studies in the gas phase show that both molecules decompose. The results show an energy landscape of plasmonically generated hot charges and its relation to probe molecule structure.

CPP 40.8 Thu 12:30 MA 141

Light-driven hydrogen evolution at copper surfaces: machine-learning accelerated nonadiabatic dynamics light the way — ●ALEXANDER SPEARS, WOJCIECH STARK, and REINHARD J. MAURER — University of Warwick, Coventry, United Kingdom

Light-induced ultrafast dynamics entail the energy transfer between light, electrons, and phonons at interfaces. Whether or not this energy transfer can be harnessed to selectively drive photocatalytic processes remains an open question. Machine-learning interatomic potentials based on electronic structure theory enable the efficient statistical sampling of chemical dynamics at metal surfaces. Molecular dynamics with electronic friction (MDEF) provide a fully anharmonic mixed quantum-classical description of electron-phonon coupling, whereby electronic friction is usually approximated with a free electron gas model. This method has previously been used to model state-resolved scattering experiments or in the calculation of vibrational lifetimes af-

ter femtosecond laser pulses, though its validity has yet to be fully assessed. Herein, we present ML-enabled MDEF simulations of thermal and light-driven hydrogen recombination and desorption probabilities from various copper surface facets. We compare results based on electronic friction based on first-order response theory and the free electron gas model and analyse the ability of different approximations to accurately describe the non-adiabatic energy transfer between the surface and adsorbates. Our approach also allows us to study the role of quantum nuclear effects on the dynamics of light-driven associative desorption.

CPP 40.9 Thu 12:45 MA 141

Strong Light-Matter Interaction to Control Plasmonic Catalysis — ●CHRISTIAN SCHÄFER, JAKUB FOJT, and PAUL ERHART — Department of Physics, Chalmers University of Technology, 412 96 Göteborg, Sweden

Optically excited nanoplasmonic particles are efficient catalysts, for which an intricate interplay of internal carrier generation and heat drives the reactions of molecules in close proximity. Here, we establish a connection between optical strong coupling between resonator structures and the nanoplasmonic plus molecule system to non-intrusively control the optical excitation energy. Based on a theoretical description from first principles (1,2,3), we demonstrate that this non-intrusive control can be used to optimize carrier injection into the molecule and thus improves plasmonic catalysis. We discuss current limitations, future development, and the prospects of strong coupling modified plasmonic catalysis.

[1] C. Schäfer and G. Johansson, PRL 128, 156402 (2022). [2] C. Schäfer, J. Phys. Chem. Lett. 2022, 13, 6905-6911. [3] C. Schäfer, J. Fojt, P. Erhart, in progress (2024).

CPP 40.10 Thu 13:00 MA 141

Anisotropic core-shell particles in the strong coupling regime — ●MATHIS NOELL and CARSTEN HENKEL — Universität Potsdam, Institut für Physik und Astronomie, Germany

Plasmonic particles coated with resonant organic absorbers (e.g., J-aggregates) provide a versatile platform to observe strong coupling. Calculations using Mie theory result, however, in the prediction of a “spurious” unobserved absorption peak between the upper and lower polariton [1]. The spurious resonance was previously thought to be caused by a negative value of the shell permittivity [2]. Alternatively, recent literature has shown that power broadening of the exciton transition efficiently suppresses the spurious resonance [3]. We demonstrate, using a modified Tavis-Cummings model, that the assumption of an isotropic shell material leads to the excitation of plasmonic dark modes (PDM) by an external field and, consequently, to an absorption line located between the upper and lower polariton. Anisotropic transition dipoles with a fixed orientation relative to the particle surface can fully suppress the coupling between the PDM and the illumination field.

[1] T. Uwada, R. Toyota, H. Masuhara, and T. Asahi, J. Phys. Chem. C 111 (2007) 1549.

[2] T. J. Antosiewicz, S. P. Apell, and T. Shegai, ACS Photonics 1 (2014) 454.

[3] F. Stete, W. Koopman, G. Kewes, C. Henkel, O. Benson, and M. Bargheer ACS Photonics 10 (2023) 2511.