Nanoscale Science and Technology
Room 114 - Session NS2-MoA

Light-Matter Interactions at the Nanoscale

Moderator: Nikolai Klimov, NIST

4:00pm **NS2-MoA-11 Time-Resolved Photoemission Electron Microscopy Imaging of the Near-Field Dynamics in Silver Nanowires Excited by Few-Cycle Short-Wave Infrared Pulses***, **Nelia Zaiats,*** Lund University, Sweden

Ultrafast photoemission electron microscopy (PEEM) is a powerful technique for studying the dynamics of surface plasmons and other electronic excitations, allowing space and time coherent imaging of plasmonic phenomena at the sample, irradiated by pulsed light with high temporal and spatial resolution [1].

Short-wave infrared (SWIR) light is used for optical communication as well as in a wide range of sensor applications [2]. Femtosecond SWIR sources can also be used for generating high-order harmonics in the water window [3]. Silver nanowires, which can be synthesized with high crystal perfection [4], present a pronounced plasmonic resonance in the SWIR range, allowing them to act as efficient light concentrators. While detailed interferometric time-resolved photoemission electron microscopy (ITR-PEEM) measurements have been carried out on Ag nanoparticles in the visible and near-infrared range [5,6], few such PEEM studies have been reported in the SWIR range [1].

Here, we investigate the near-field dynamics in Ag nanowires excited by SWIR pulses with a duration of ~17 fs (2.3 optical cycles) and wavelengths in the 1600-2400 nm range using ITR-PEEM. We study the nanowire response for different light polarizations and intensities as well as for different orientations and geometrical shapes of the wires. We excite the dipolar longitudinal plasmon mode of the nanowire and investigate the near-field dynamics on the femtosecond time scale using two SWIR pump-probe pulses separated in time. The study shows the use of ITR-PEEM in the SWIR wavelength regime, revealing the dynamics of a model plasmonic system.

References

[1] E. Mårsell, et al. Photoemission electron microscopy of localized surface plasmons in silver nanostructures at telecommunication wavelengths, J. of Appl. Phys. 117, 083104 (2015).

[2] M. P. Hansen and D. S. Malchow "Overview of SWIR detectors, cameras, and applications", Proc. SPIE 6939, Thermosense XXX, 69390I (2008).

[3] J. Li, J. Lu, A. Chew, et al. Attosecond science based on high harmonic generation from gases and solids. Nat Commun 11, 2748 (2020).

[4] M. Mayer, et al. Controlled Living Nanowire Growth: Precise Control over the Morphology and Optical Properties of AgAuAg Bimetallic Nanowires. Nano Lett 15(8), 5427 (2015).

[5] D. Bayer, et al. Time and Space Resolved Studies on Metallic Nanoparticles. In: D.T. Cat, A. Pucci, K. Wandelt. (eds) Physics and Engineering of New Materials. Springer Proceedings in Physics 127. Springer, Berlin, Heidelberg (2009).

[6] E. Mårsell, et al. Nanoscale imaging of local few-femtosecond near-field dynamics within a single plasmonic nanoantenna, Nano Lett 15(10), 6601 (2015).

4:15pm **NS2-MoA-12 AFM-IR of EHD-Printed PbS Quantum Dots: Quantifying Ligand Exchange at the Nanoscale***, L. Ferraresi, G. Kara,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; **Nancy Burnham,*** Worcester Polytechnic Institute*; R. Furrer, D. Dirin, F. La Mattinia, M. Kovalenko, M. Calame, I. Shorubalko,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland

Colloidal quantum dots (cQDs) recently emerged as building blocks for semiconductor materials with tuneable properties. Electro-hydrodynamic printing can be used to obtain sub-micrometre patterns of cQDs without elaborate and aggressive photolithography steps. Post-deposition ligand exchange is necessary for the introduction of new functionalities into cQD solids. However, achieving a complete bulk exchange is challenging and conventional infrared spectroscopy lacks the required spatial resolution for its analysis. Infrared nanospectroscopy (AFM-IR) enables quantitative analysis of the evolution of vibrational signals and structural topography on the nanometre scale upon ligand substitution on lead sulphide (PbS) cQDs. A solution of ethane-dithiol in acetonitrile demonstrated rapid (~60 s) and controllable exchange of more than 80% of the ligands, encompassing structures up to ~800 nm in thickness. Prolonged exposures (>1 h) led to the degradation of the microstructures, with a systematic removal of cQDs regulated by surface-to-bulk ratios and solvent interactions. This study establishes a method for the development of devices through a combination of tuneable photoactive materials, additive manufacturing of microstructures, and their quantitative nanometre-scale analysis.

4:30pm **NS2-MoA-13 AVS National Student Awardee Talk: Slow and Fast Timescale Effects of Photoinduced Surface Oxygen Vacancies on the Charge Carrier Dynamics of TiO_2***, **Bugrahan Guner**[1]**, O. Dagdeviren,*** École de technologie supérieure, University of Quebec, Canada

The migration of charge carriers (*e.g.*, electrons, holes) in metal oxides, such as TiO_2, plays a vital role in (photo)catalytic applications [1]. Nevertheless, photoinduced surface oxygen vacancies (PI-SOV) scan significantly alter the dynamics of charge carriers [2-4]. Here, we study the effect of PI-SOVs (prompted by high-energy ultraviolet irradiation) on fast (*i.e.*, electrons) and slow (*i.e.*, holes) charge carriers via time-resolved atomic force microscopy (TR-AFM) measurements, while simultaneously exploring the effect of gold nanoparticles (Au-NPs). We conducted our measurements on Au-NP-deposited titanium dioxide, *i.e.*, TiO_2. Our measurements illustrate that the induced oxygen vacancy (V_O) defects result in a decrease in time constants associated with the migration of electrons. In addition, we quantified the effect of induced defectson the migration barrier of slow charge carriers, *i.e.*, holes. Our respective measurements show that PI-SOVs lower the migration barrier of holes for both the TiO_2 and TiO_2/Au-NP interface. We believe that the observed statistical difference is caused by the effect of defects over the recombination and trapping mechanisms of fast and slow charge carriers. Our results express the important effect of V_O on charge migration dynamics, which underlines the need for further studies of defects under realistic conditions.

[1] Bugrahan Guner, Orcun Dincer, and Omur E. Dagdeviren, ACS Applied Energy Materials **7** (6), 2292 (2024).

[2] Bugrahan Guner, Simon Laflamme, and Omur E. Dagdeviren, Review of Scientific Instruments **94** (6) (2023).

[3] Bugrahan Guner and Omur E. Dagdeviren, ACS Applied Electronic Materials **4** (8), 4085 (2022).

[4] Orcun Dincer, Bugrahan Guner, and Omur E. Dagdeviren, APL Materials **12** (2) (2024).

Funding information:

This work was supported by the Canada Economic Development Fund, Natural Sciences and Engineering Research Council of Canada, and Le Fonds de Recherche du Québec - Nature et Technologies.

4:45pm **NS2-MoA-14 Improving the Shape and Optical Stabilities of Plasmonic Au Nanobipyramids by Metal Shell Deposition***, **Thomas Egan,** G. Chen,* University of Central Florida

Anisotropic plasmonic metal nanoparticles show significant promise as light-sensitizing components in the design of advanced optical materials. Their plasmon resonances can be tuned across the visible and near-IR regions by adjusting their aspect ratio, allowing them to harvest solar energy well below the bandgaps of conventional semiconductors. However, their processing and applications under environmental conditions often involve elevated temperatures, which may cause restructuring and shape change of the anisotropic plasmonic metal nanoparticles and lead to a shift of their plasmon resonances. Therefore, it is necessary to improve their thermal stability for robust applications. Here, using anisotropic Au nanobipyramids (NBPs) immobilized on a TiO_2 support as a model system, we demonstrate that the deposition of thin shells of different metals (Au@M NBPs, M = Ag, Pd, Pt) can alter and drastically increase their thermal stability. For pure Au NBPs and Au@Ag NBPs, their tips are observed to progressively blunt and their plasmon resonances begin to blue-shift when annealed at 100 ℃ for 1 hour, while the shapes and plasmon resonances of Au@Pd and Au@Pt NBPs are well-maintained up to 200 ℃ and 250 ℃, respectively. Notably, we also find that the thermal stability of Au@Pd and Au@Pt NBPs is unaffected by annealing up to 4 hours, suggesting that this method can be used to protect metal nanoparticles under various operating conditions. We further use energy-dispersive X-ray (EDX) spectroscopy to map the alloying processes of these

[1] **AVS National Student Awardee**

core@shell NBPs, which reveal that the onset temperature of alloying increases as the lattice mismatch between core and shell metals increases.

5:00pm **NS2-MoA-15 Photonic Chip Packaging for Extreme Environments**, ***Nikolai N Klimov***, *S. Robinson,* National Institute for Science and Technology (NIST)*; A. Rao,* National Institute for Science and Technology (NIST); University of Maryland*; D. Barker, F. Bateman, G. Holland, D. Westly,* National Institute for Science and Technology (NIST)

Integrated photonic sensors have advanced significantly in the past decade, driven by a combination of the inherent scalability of integrated photonics combined with precision nanofabrication as well as an ever-increasing range of applications. Such integrated sensors offer advantages in size, weight, and power compared to traditional sensor form-factors. While photonic packaging is well established for many applications, robust and ruggedized photonic packaging is indispensable to field-deployable photonic sensors that must operate under extreme environments. Here, we demonstrate a method for photonic packaging that can operate at cryogenic temperatures as well as in high radiation environments. We also assess the feasibility of the bonding method for high-temperature applications. Using low temperature hydroxide catalysis bonding and a custom packaging station to actively align and attach optical fiber v-groove arrays to a silicon photonic chip, we characterize the packaged chip across a wide temperature range from 360 K down to 3.8 K, confirming suitability for cryogenic operation, and observe < 1 dB variation per grating coupler across a 50 nm wavelength range. Moreover, we expose our packaged chip to an electron beam corresponding to an accumulative radiation dose of 1.1 MGray and observe no degradation in insertion loss across 1510 nm to 1630 nm wavelength range. Finally, we bond several dies and confirm the high temperature compatibility of our bonding approach by observing no change in mechanical bond strength before and after annealing at 973 K. Our packaging methodology can be readily adapted to different photonics applications, ranging from cryogenic circuits to deployable extreme-environment sensors.

5:15pm **NS2-MoA-16 Periodic and Quasi-Periodic Plasmonic Architectures for Strong Light-Matter Interaction**, *M. Ferrera, V. Aglieri, J. Pelli Cresi,* Istituto Italiano di Tecnologia, Italy*; E. Ghidorsi,* Istituto Italiano di Tecnologia, Dipartimento di Fisica, Università degli Studi di Genova, Italy*;* ***Andrea Toma****,* Istituto Italiano di Tecnologia, Italy

Light-matter interaction pervades our everyday life and typically involves an energy exchange between an external electromagnetic field and a photon emitter (dye molecules, quantum dots, etc.). Usually, this interaction is rather weak and such that only the spontaneous emission rate is modified. However, the engineering of nanohybrid architectures can promote an energy exchange rate between light and matter faster than any relaxation process. Under these conditions, the system can enter the strong-coupling regime and new hybrid light-matter states, called polaritons, are formed, with potential interest in various fields spanning from photocatalysis to optoelectronic and quantum technologies [1].

For the realization of functional polaritonic devices, particular interest has been devoted towards the integration of quantum emitters with periodic structures supporting collective modes, such as surface plasmon polariton Bloch waves or surface lattice resonances. These resonance features can be properly controlled by acting on the design of the photonic architecture. Among the various possibilities, the exploitation of photonic metamaterials lacking periodic translational order (e.g. quasicrystals) can significantly increase the design degrees of freedom of the photonic component thus offering interesting perspectives in the development of novel hybrid platforms [2]. Here, the focus is on strongly-coupled systems in which quantum emitters are integrated with both periodic and quasi-periodic two-dimensional plasmonic crystals. The radiative properties of the heterostructures along with their intrinsic photophysics were investigated by means of both steady-state and time-resolved optical spectroscopies [3,4]. This work is stimulating toward a further exploration on the symmetry-dependent properties of long-range ordered 2D arrays, with a particular focus on their peculiar near-field distribution. More in general, the presented results can set the stage for the realization of novel polaritonic devices with tailored properties for specific applications, such as photocatalysis.

Acknowledgement

This work is part of the REPLY project that received funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation program (grant agreement No 101002422).

References

[1] F. J. Garcia-Vidal, *et al.* Science 373, eabd0336 (2021); [2] S. Yu, *et al.* Nat. Rev. Mater. 6, 226 (2020); [3] H. Wang, *et al.* Adv. Opt. Mater. 5, 1600857 (2017); [4] H. Wang, *et al.* Adv. Funct. Mater. 28, 1801761 (2018).

Author Index

Bold page numbers indicate presenter