Nano and 2D Materials
Room Naupaka Salon 4 - Session NM2-WeM

Properties of 2D Materials
Moderator: Zbynek Novotny, Pacific Northwest National Laboratory

10:20am **NM2-WeM-8 Atomic-Scale Control of Plasmon-Driven Single-Molecular Switch***, Akitoshi Shiotari,* Fritz-Haber Institute, Germany**INVITED**

Localized surface plasmons provide effective molecule–light interactions that are highly motivating for the realization of advanced molecule-based optoelectronic devices [1]; however, innovative precision in plasmon control is still required to induce local selective reactions at the single- or sub-molecule level. Scanning tunneling microscopy (STM) using a plasmonic metal tip not only creates a local photochemical reaction field, but also enahnces Raman signals from molecules within the STM junction, namely tip-enhanced Raman spectroscopy (TERS). Low-temperature STM-TERS is a powerful tool to evaluate the structure and photoreactivity of single molecules, even on a semiconductor silicon surface [2].

In this talk I will mainly report on a plasmon-induced single-molecule switch in a Ag-tip–anhydride-molecule–Si-surface junction characterized and controlled by low-tempearture STM-TERS [3]. The localized surface plasmon at the tip can dissociates of the O–Si bonds between the molecule and the Si(111)-7x7 surface, resulting in the conductance switching between OFF (tunnelling) and ON (point-contact) states of the tip–adsorbate junction. Sub-angstrom scale positioning of the plasmonic tip over the target molecular can tune the switching rate. We also demonstrated that the switching ability can be changed by the single-atom-level substitution of the molecular structure; imide/Si(111) is inert against the tip plasmon. Our demonstrations of the tip-plasmon control and the chemical tailoring for the single-molecule switch pave the way to the fusion of single-molecule electronics and plasmonics, towards ultimate minitualization of optoelectronics, namely "pico-optoelectronics."

Reference:

1. Xiaona Xu, Chunyan Gao, Ramya Emusani, Chuancheng Jia, and Dong Xiang, *Adv. Sci.* 2400877 (2024) DOI: 10.1002/advs.202400877
2. Borja Cirera, Shuyi Liu, Youngwook Park, Ikutaro Hamada, Martin Wolf, Akitoshi Shiotari, and Takashi Kumagai, *Phys. Chem. Chem. Phys.* (2024) DOI: 10.1039/d4cp01803f.
3. Youngwook Park, Ikutaro Hamada, Adnan Hammud, Takashi Kumagai, Martin Wolf, and Akitoshi Shiotari, *Nat. Commun.* (2024) DOI: 10.1038/s41467-024-51000-w.

11:00am **NM2-WeM-10 Tunable Metasurface with Gap and Collective Surface Plasmon Modes***, Anatoliy Pinchuk,* University of Colorado at Colorado Springs

We investigate a tunable metasurface composed of a monolayer of gold nanoparticles on a glass substrate in close proximity to a thin aluminum film, both numerically and experimentally. The extinction spectra of the metasurface exhibit three angle- and polarization-dependent peaks. Using the finite-difference time-domain (FDTD) method, we confirm the positions of both the collective surface plasmon and gap modes. Altering the polarization of the incident light causes a shift in the wavelength of these peaks.

A recent study reported strong coupling between the gap and collective surface plasmon polariton modes in a system consisting of a monolayer of gold nanoparticles supported on a glass substrate, separated from a thin aluminum film by a shellac polymer spacer film of varying thickness [1,2]. Two optical extinction bands were identified: a long-wavelength gap mode and a short-wavelength collective surface plasmon mode. The position and amplitude of both modes were found to depend strongly on the thickness of the shellac dielectric spacer. Varying the spacer thickness causes a shift in the two modes and their degeneration into a single mode as the thickness increases. These findings reveal a complex interplay between the gap and collective surface plasmon polariton modes.

Despite detailed numerical and experimental studies on various geometries of plasmonic metasurfaces, all such studies have been conducted with the probing light beam incident normally. There have been no reports on the polarization dependence of the extinction spectra for monolayers of gold nanoparticles in close proximity to a thin metal film. Our study addresses this gap by exploring the effects of polarization on the optical properties of these metasurfaces, providing new insights into their tunable characteristics and potential applications in nanophotonic devices.

References

1. Yeshchenko, O.A., Kozachenko, V.V., Tomchuk, A.V., Haftel, M., Knize, R.J., and Pinchuk, A.O. “Plasmonic metasurfaces with tunable gap and collective surface plasmon resonance modes,” The Journal of Phys. Chem. C, Vol. 123, No. 20, 13057-13062, 2019.

2. Yeshchenko, O. A., Kozachenko, V. V., Naumenko, A. P., Berezovska, N.I., Kutsevol, N.V., Chumachenko, V.A., Haftel, M., Pinchuk, A.O., “Gold nanoparticle plasmon resonance in near-field coupled Au NPs layer/Al film nanostructure: Dependence on metal film thickness,” Photonics and Nanostructures- Fundamentals and Applications, Vol.29, 1-7, 2018.

11:20am **NM2-WeM-11 Probing Inherent Optical Anisotropy in Transition Metal Dichalcogenide Substrates via Mie Scattering-Induced Surface Analysis (MISA)***, Hwi Je Woo,* Korea Research Institute of Standards and Science, Republic of Korea*; Jaewon Han, Sangmin Ji, Bong Gyu Shin,* Sungkyunkwan University (SKKU), Republic of Korea*; Sung-Gyu Lee,* Nanyang Technological University, Singapore*; **Young Jae Song**,* Sungkyunkwan University (SKKU), Republic of Korea

We present a novel approach to investigate the optical anisotropy of transition metal dichalcogenide (TMD) substrates using Mie scattering-induced surface analysis (MISA). By employing scattering-type scanning near-field optical microscopy (s-SNOM) and finite-difference time-domain (FDTD) simulations, we systematically studied and directly visualized the Mie scattering patterns of superspherical gold nanoparticles (s-AuNPs) at the nanoscale.

Our research revealed distinct differences in the optical properties of molybdenum disulfide (MoS2) and rhenium disulfide (ReS2) substrates. While MoS2 exhibited optical isotropy, ReS2 demonstrated significant anisotropic behavior, particularly in the near-infrared energy range. This anisotropy was manifested through more pronounced spectral and angular responses in the satellite peaks of Mie scattering patterns.

We observed that the distances between satellite peaks in the Mie scattering patterns varied with the incident angle of light for ReS2, but remained constant for MoS2. This angular dependence in ReS2 was consistently observed across different excitation energies, providing strong evidence of its inherent optical anisotropy.

Our findings highlight the potential of MISA as a powerful, non-destructive tool for probing the intrinsic dielectric properties of substrates at the nanoscale. This technique offers superior visualization of nanoscale anisotropies and enables a more nuanced approach to substrate characterization compared to traditional spectroscopic methods.

The insights gained from this study not only advance our understanding of light-matter interactions at the nanoscale but also have significant implications for the development of advanced nanophotonic devices and the field of optical metrology.

Keywords: superspherical-AuNP, scattering-type scanning near-field optical microscope, Mie scattering, anisotropy, substrate

11:40am **NM2-WeM-12 Enhancement of Photocatalytic Water Splitting Upon Induced Structural Evolution and Increase of Phase Polarity of Two-Dimensional Covalent Organic Frameworks***, Jrjeng Ruan,* National Cheng Kung University (NCKU), Taiwan

The evolution of smectic liquid crystals of newly designed two-dimensional covalent organic frameworks (COFs) has been disclosed for the first time. With obtained changes of phase morphology, selected-area electron diffraction patterns, and Young’s modulus via compressive testing, this smectic phase is realized to transfer to nematic phases upon the ph. changes of surrounding solutions. Furthermore, the coordination of selected metal ions for the preparation of M-COFs is also stimulated by conducted ph. changes, which is surprisingly found able to greatly adjust the out-of-plan phase polarity and thus the piezoelectric responses of evolved liquid crystals of synthesized M-COFs. The controlled adjustment of phase polarity has been clarified able to modify energy bandgap, enhance absorption of visible lights, and increase the efficiency of stimulated electron transition to metal active centers upon the absorption of visible lights. As a result, the coordination of metal ions and accompanied elevation of phase polarity significantly promote the photocatalytic water splitting via synthesized M-COF as photocatalysts. Hence, with the coordination of metal ions on evolved COF liquid crystals, this research has investigated the availability of various levels of phase polarity of M-COF

liquid crystals, and comprehensively studies achievable impacts and contributions of phase polarity on photocatalytic water splitting.

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