Atomic-Scale Optical Spectroscopy

Center for Mesoscopic Sciences
Division of Broadband Multiscale Analysis

KUMAGAI, Takashi
Associate Professor
[kuma@ims.ac.jp]

Education
2006 B.S. Ritsumeikan University
2008 M.S. Kyoto University
2011 Ph.D. Kyoto University

Professional Employment
2008 JSPS Research Fellow, Kyoto University
2011 JSPS Research Fellow, Fritz-Haber Institute
2013 Group Leader, Fritz-Haber Institute
2021 Associate Professor, Institute for Molecular Science
Associate Professor, The Graduate University for Advanced Studies
2020 Guest Professor, Hokkaido University

Awards
2013 Inoue Research Award for Young Scientists
2014 Morino Award for Molecular Science
2016 Gerhard Ertl Young Investigator Award
2020 Gaede Prize (German Physical Society)
2020 The Commendation for Science and Technology by the Minister of Education, Culture, Sports, Science and Technology
The Young Scientists' Award
2020 Heinrich Rohrer Medal (The Japan Society of Vacuum and Surface Science)

Member
Assistant Professor
NISHIDA, Jun
Secretary
ITO, Atsuko

Keywords Atomic-Scale Optical Spectroscopy, Scanning Probe Microscopy, Nanoscale Science

Optical imaging and spectroscopy at atomic resolution is an overarching goal in modern nanoscale science and technology, allowing us to directly access atomic-scale structures and dynamics in real space and real time. Atomic-scale crystal imperfections, defects and inhomogeneities indeed play a crucial role in physicochemical properties and functions of solid catalysts and semiconductor optoelectronic devices. We have challenged to attain atomic-scale optical spectroscopy by combining advanced low-temperature scanning tunneling microscopy, laser spectroscopy and nanoplasmonics.

Electromagnetic fields can be confined to nanoscale through excitation of localized surface plasmon resonances of metallic nanostructures. Plasmonics is a mature research field, enabling precise control of nanoscale light. Accordingly, nanoscale optical imaging and spectroscopy well below the diffraction limit has become a more routine technique. However, the typical spatial resolution remains a few tens of nanometers, which is still far from the atomistic length scale. More recently, state-of-the-art experiments and theories demonstrated that atomic-scale confinement of electromagnetic fields occurs at atomistic asperities existing on metallic nanostructures. However, it is an outstanding challenge to precisely manipulate atomically confined light. We have developed advanced experimental techniques to manipulate extremely confined, strong plasmonic fields in scanning tunneling microscope junctions and implemented ultrasensitive and ultrahigh resolution optical spectroscopy. We also investigate intriguing atomic-scale strong light–matter interactions in an atomically well-defined environment.

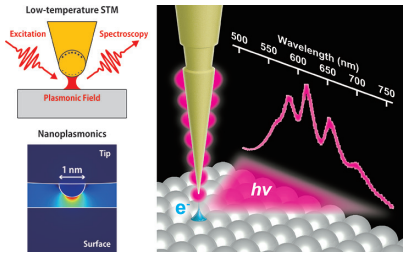

Figure 1. Atomic-scale optical spectroscopy in plasmonic scanning probe microscope junction.

Selected Publications

- S. Liu *et al.*, "Plasmon-Assisted Resonant Electron Tunneling in a Scanning Tunneling Microscope Junction," *Phys. Rev. Lett.* **121**, 226802 (2018).
- H. Böckmann, S. Liu *et al.*, "Near-Field Manipulation in a Scanning Tunneling Microscope Junction with Plasmonic Fabry-Pérot Tips," *Nano Lett.* **19**, 3597–3602 (2019).
- S. Liu *et al.*, "Resolving the Correlation between Tip-Enhanced Resonance Raman Scattering and Local Electronic States with 1 nm Resolution," *Nano Lett.* **19**, 5725–5731 (2019).
- S. Liu *et al.*, "Dramatic Enhancement of Tip-Enhanced Raman Scattering Mediated by Atomic Point Contact Formation," *Nano Lett.* **20**, 5879–5884 (2020).
- S. Liu *et al.*, "Atomic Point Contact Raman Spectroscopy of a Si(111)-7×7 Surface," *Nano Lett.* **21**, 4057–4061 (2021).
- S. Liu *et al.*, "Anti-Stokes Light Scattering Mediated by Electron Transfer Across a Biased Plasmonic Nanojunction," *Nano Lett.*, in print.

1. Control of Gap-Mode Plasmons in Scanning Tunneling Microscope Junctions

Optical imaging and spectroscopy in plasmonic scanning tunneling microscope junctions rely on gap-mode plasmons whose properties are largely determined by the nanoscale morphology of the tip apex. Although a metallic tip for a scanning tunneling microscope is typically prepared by electrochemical etching, it is hard to precisely control the nanoscale structure of its apex. In order to obtain plasmonic tips in a highly controlled and reproducible manner, we employed focused ion beam milling.[1] Figure 2a displays a scanning electron micrographs of a gold tip with a nanoscopically sharpened apex. Furthermore, we demonstrated that the spectral features of the gap-mode plasmon can be controlled by making nanoscale structures on the tip shaft. As an exemplary case, we produced nanoscopically sharp gold tips with a single groove on the shaft at a distance of a few micrometers from the apex. This structure leads to tunable plasmonic Fabry–Pérot interference. Figures 2b and 2c show the electrodynamic simulation and the scanning tunneling luminescence spectra, respectively, where the modulated spectral response through the interference is observed. Nanofabrication of plasmonic tips will be a key technology to attain highly precise, reproducible nanoscale and atomic-scale optical imaging and spectroscopy.

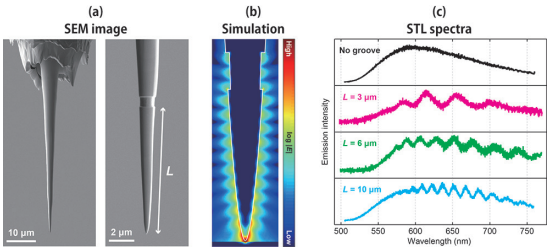

Figure 2. Nanofabrication of plasmonic tip with focused ion beam milling. (a) Scanning electron micrograph of a nanoscopically sharpened gold tip. (b) Simulation of plasmonic Fabry–Pérot tip. (c) Scanning tunneling luminescence spectra of the plasmonic Fabry–Pérot tip.

2. Ultrasensitive and Ultrahigh Resolution Tip-Enhanced Raman Spectroscopy

Raman spectroscopy is a versatile tool widely used in physics, chemistry and biology. Low-temperature tip-enhanced Raman spectroscopy (TERS) enables chemical identification with single-molecule sensitivity and with extremely high spatial resolution even down to the atomic scale.[2,3] The large enhancement of Raman scattering obtained in TERS originates from electromagnetic field and/or chemical enhancement mechanisms. Whereas former enhancement requires a strong near-field through excitation of localized surface plasmons, the latter is governed by resonance in the electronic structure of the sample, known as resonance Raman spectroscopy. Recently we demonstrated tip-enhanced resonance Raman scattering (TERRS) for ultrathin ZnO films epitaxially grown on a Ag(111) surface,[4] where both electromagnetic and chemical enhancement mechanisms are simultaneously operative, yielding exceptionally high sensitivity. By recording scanning tunneling spectroscopy (STS) in parallel, we also showed that the TERRS intensity is strongly correlated with the nanoscale variation of the electronic resonance. It was found that the spatial resolution of TERRS is dependent on the tip–surface distance and reaches nearly 1 nm in the tunneling regime. This exceptionally high resolution can be rationalized by the extreme confinement of the plasmonic field in the junction. Simultaneous STS and TERRS mapping visualize a correlation between the local electronic resonance and the Raman spectrum at near-atomic resolution. Therefore, TERRS will pave the way to directly observe electron–phonon coupling on the atomic length scale.

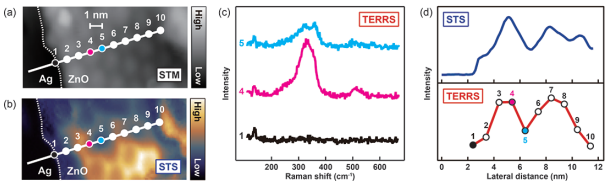

Figure 3. Tip-enhanced resonance Raman spectroscopy of ultrathin zinc oxide films. (a) and (b) STM and STS images of ultrathin zinc oxide film. (c) TERRS spectra obtained at different locations over the zinc oxide film. (d) STS and TERRS intensities along the line indicated in (a) and (b).

Additionally, we discovered that tip-enhanced Raman scattering can be dramatically enhanced through formation of atomic point contacts.[5,6] We showed that atomic point contact formation between a silver tip and the surface of a bulk Si sample can lead to the dramatic enhancement of Raman scattering and consequently the phonon modes of the reconstructed Si(111)-7×7 surface can be detected. Furthermore, we demonstrate the chemical sensitivity of this method by probing local vibrations resulting from Si–O bonds on the partially oxidized Si(111)-7×7 surface. This approach will expand the applicability of ultrasensitive tip-enhanced Raman spectroscopy, exceeding the previous measurement strategies that exploit intense gap-mode plasmons, typically requiring a plasmonically resonant substrate.

References

1) H. Böckmann, S. Liu *et al.*, *Nano Lett.* **19**, 3597 (2019).
2) J. Lee *et al.*, *Nature* **568**, 78 (2019).
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4) S. Liu *et al.*, *Nano Lett.* **19**, 5725 (2019).
5) S. Liu *et al.*, *Nano Lett.* **20**, 5859 (2020).
6) S. Liu *et al.*, *Nano Lett.* **21**, 4057 (2021).

Awards

KUMAGAI, Takashi; Gaede Prize (German Physical Society) (2020).
KUMAGAI, Takashi; Heinrich Rohrer Medal (The Japan Society of Vacuum and Surface Science) (2020).