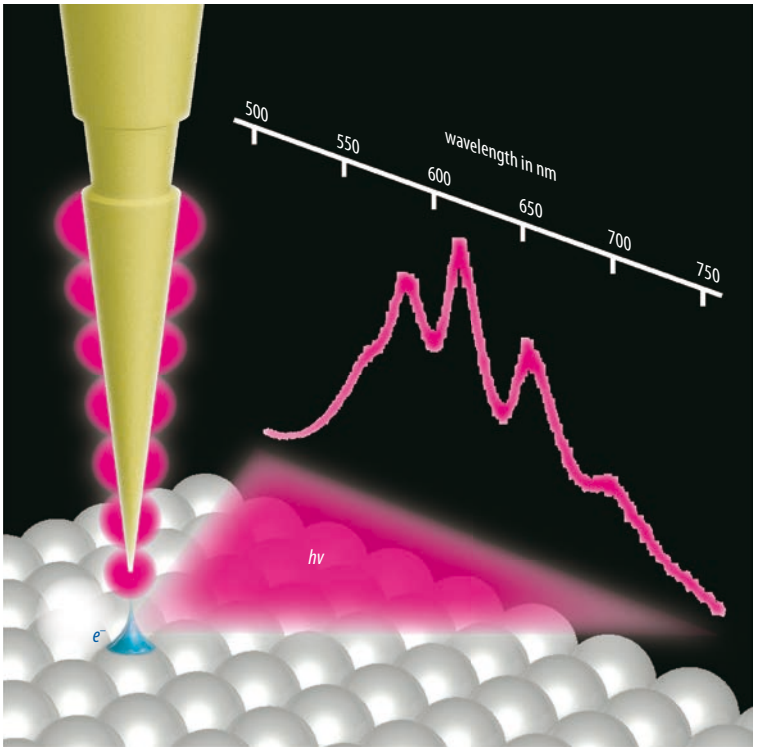
GAEDE-PREIS

Turn on Nanolight in a Tiny Gap

Photophysical and photochemical phenomena are directly observable using low-temperature scanning tunneling microscopy combined with plasmonics.

Takashi Kumagai

Nanolight originates from localized surface plasmon excitation in metallic nanostructures. It possesses great potential for local optical spectroscopy down to the single-molecule level and for the enhancement of photophysical and photochemical processes such as solar energy conversion and photocatalytic reactions. Sophisticated experiments combine scanning tunneling microscopy with laser optics and allow the direct investigation of the microscopic mechanisms of nanolight-driven phenomena in plasmonic nanogaps. In addition, it is possible to perform optical spectromicroscopy at an unprecedented spatial resolution.



Confining light into a small volume enhances the interaction of light and matter. Versatile applications range from imaging and spectroscopy to optoelectronic devices and photocatalysis. With conventional optics, the spatial confinement of light is limited to a few hundred nanometers due to the diffraction limit. To realize a further confinement and to turn on "nanolight", metallic nanostructures can generate localized electromagnetic fields at the nanoscale through collective electron oscillations, so-called surface plasmons [1]. If a localized surface plasmon resonance efficiently couples to propagating light, the electromagnetic fields are confined to a sub-wavelength scale.

The advancement of highly precise fabrication techniques of metallic nanostructures has fueled the rapid growth of plasmonics and nanophotonics in the last few decades [2]. Plasmonic nanogaps formed between metallic nanoparticles are of particular interest to fundamental physics and applications because of an extreme field enhancement (**Fig. 1a**). They enable single-molecule detection as well as an enhancement of photophysical and photochemical processes by orders of magnitude. However, the direct observation of plasmon-induced phenomena in such tiny gaps remains challenging because conventional microscopy and spectroscopy can't uncover the microscopic structures and dynamics in detail due to insufficient spatial resolution.

We have developed experimental techniques to combine a low-temperature scanning tunneling microscope with laser optics in order to perform local optical excitation and spectroscopy at the level of a single atom or molecule in plasmonic junctions. The illumination of plasmonic scanning tunneling microscope junctions can also lead to a strong field enhancement and confinement (**Fig. 1b**). Low-temperature scanning tunneling microscopy offers not only atomic-resolution imaging, but also local electronic, vibrational and spin spectroscopy as well as single-atom and molecule manipulation. Therefore, this approach can elucidate fundamental mechanisms behind plasmon-driven phenomena on the atomic and molecular level.

If one wants to investigate nanolight-driven phenomena and to perform highly reliable scanning near-field optical microscopy in plasmonic nanojunctions, it is necessary to control the nature of near fields generated by localized surface plasmon excitation. To this end, the shaping of tips provides spectral tunability because the geometry of metallic nanostructures as well as the material of the tip largely modify the plasmonic response. In order to produce very sharp tips with nanoscale precision (**Fig. 2a**), we have developed a nanofabrication method using a focused ion beam. Focused ion-beam milling is a very powerful nanofabrication technique and allows us to "sculpture" various tip structures, thus, engineering the localized surface plasmon properties of the tips.

As a simple example of localized surface plasmon engineering, we demonstrated a spectral modulation using

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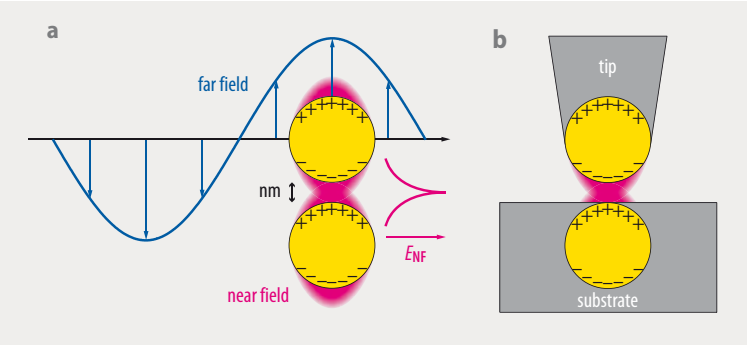

Fig. 1 A localized surface plasmon excitation in a nanoparticle dimer (a, yellow) is separated by a few nanometers. The incoming light (blue) stimulates corrective oscillations of electrons in the nanoparticles generating a highly localized and intense electromagnetic field (pink) in the gap. A scanning tunneling microscope junction might generate a localized surface plasmon (b). This nanolight is spatially controlled by scanning the plasmonic tip.

plasmonic Fabry-Pérot resonance by producing a sharp Au tip with a single groove on its shaft [3]. Scanning tunneling luminescence spectroscopy determines the spectral response of the Fabry-Pérot tip. Thus, inelastic electron tunneling excites the localized surface plasmon resonance in the scanning tunneling microscope junction and photon emission is detected in the far field [4]. The Fabry-Pérot tip exhibits modulated spectra resulting from interference between localized and propagating surface plasmon modes that forms a standing wave on the shaft (**Fig. 2b**). As expected, the peak spacing in the modulated spectra becomes smaller when the distance between the tip apex and the groove gets larger (**Fig. 2c**). We further demonstrated that an optimized tip shape improves the quality factor of the plasmonic Fabry-Pérot interference [3]. Nanofabrication of plasmonic tips will be a basic technology to achieve highly precise and reproducible atomic-scale optical spectroscopy.

Nanolight-driven resonant electron transfer

Light-driven electron transfer is an important elementary process in energy and material conversions such as photovoltaics and photocatalysis. Here, visible light induces efficient carrier generation and transfer which is of particular interest to make use of solar energy. We discovered a novel plasmon-assisted resonant electron transfer in a simple model system [5]. Rydberg-like electronic states exist over a single-crystal Ag(111)-surface, so-called field emission resonances (**Fig. 3a**), and electrons in the tip can resonantly tunnel these states through the vacuum gap [6]. The field emission resonances can be observed in scanning tunneling spectroscopy. When the bias voltage V_{bias} is swept, the field emission resonances appear as a series of characteristic peaks (**Fig. 3b**). Without illumination, the peaks in the conductance spectrum correspond to the respective levels of the field emission resonances (**Fig. 3c**). The first peak occurs near the work function of the surface Φ_s and the potential gradient in the junction determines the peak spacing of higher-order resonances.

A localized surface plasmon in transition supports resonant electron transfer from the tip to the surface with continuous illumination at a resonant wavelength. This process results in a significant red-shift of the characteristic peaks in the scanning tunneling spectra. We found that the shift of the first peak is equal to the incident photon energy, i.e., about 1.9 V for 633 nm and about 2.3 V for 532 nm (**Fig. 3d**). The field emission resonances can be used to investigate excited electron dynamics at metal surfaces [7]. In the future, the ultrashort optical excitation of plasmon scanning tunnelling microscope transitions will make it possible to understand ultrafast electron dynamics at the atomic level.

Nanolight-driven chemical reaction

Nanolight also drives photochemical reactions, which offer great potential for efficient material conversion using solar energy [8]. Such "plasmonic catalysis" may create new and more selective reaction pathways which cannot be realized by thermal-driven catalysis [9]. The plasmon-induced reactions happen in nanogaps, so-called "hot stops". Here a strong field amplification occurs, but the process is difficult to observe directly at the molecular level. A microscopic understanding of plasmon-driven reactions will provide valuable insights into the rational design of plasmonic catalysts. We demonstrated that the scanning tunneling microscope junction allows direct observation of plasmon-

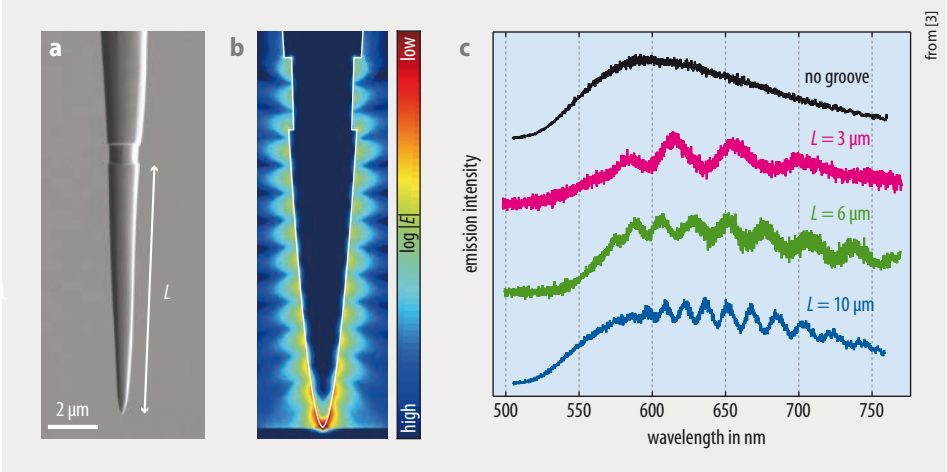

Fig. 2 Focused ion-beam milling produces Au tips with a single groove on their shafts at a distance *L* to the apex of the tip (a, scanning electron micrograph). The scanning tunneling luminescence varies due to the plasmonic Fabry-Pérot interference (b, simulation). The emission spectra depend on the distance *L* between groove and apex (c).

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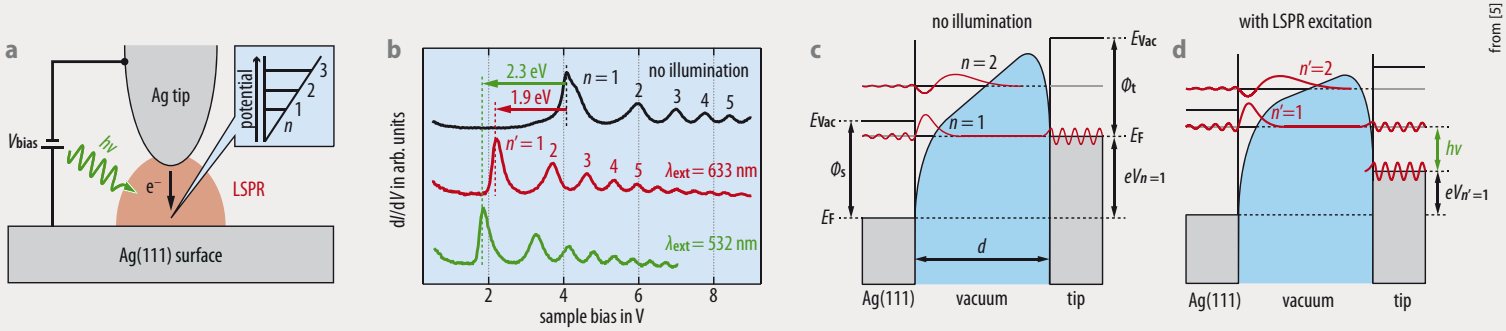

Fig. 3 Plasmon-assisted resonant electron tunneling is examined in the junction of the Ag tip and the Ag(111) surface (a). The field emission resonance spectra change with and without illumination and depend on the wavelength λ_{ext} (b). The variations stem from the corresponding potential in the junction (blue area in c, d) and the different incident photon energy (E_F: Fermi level, E_{vac}: vacuum level, $\Phi_{s(t)}$: work function of surface (tip), d: gap distance, $n(n')$: index of the resonances, $V_{n(n')}$: voltage of the resonances, hv: incident photon energy).

driven reactions [10, 11]. A plasmon-induced single-molecule tautomerization of porphycene on a Cu(110) surface at 6 K serves as an example. Porphycene switches between two cis configurations in response to a localized surface plasmon excitation in the junction (**Fig. 4a**). The scanning tunneling microscopy signal monitors in real-time a random telegraph noise between the two states (**Fig. 4b**, inset). Hot carriers, generated in the tip and on the surface through the Landau decay of the excited localized surface plasmon, induce the reaction. Such non-equilibrium hot carriers are subsequently transferred to adjacent semiconductors or molecules and play a crucial role in photovoltaic and photocatalytic applications [12]. There is therefore a growing interest in elucidating how differences in the electronic structure as well as in the optical reaction of metallic nanostructures influence the dynamics [13].

A wavelength-tunable laser source enables us to investigate the spectral response of the reaction cross section. Therefore, we call the method near-field action spectroscopy [10]. If the near-field action spectrum is recorded with a plasmonic Fabry-Pérot tip, a modulated spectral response appears (**Fig. 4b**). This modulation demonstrates that the molecule acts as a nanoscale sensor to detect the field enhancement in the junction. Near-field spectral response of metallic nanogaps is a key characteristic in plasmon-assisted photophysical and photochemical processes. Our approach will provide a new way to examine microscopic mechanisms of plasmon-driven chemical reactions.

Vibrational spectromicroscopy by nanolight

Nanolight allows ultrasensitive nanoscale optical spectromicroscopy. The idea of near-field optical microscopy – enabling optical spectroscopy with deep subwavelength spatial resolution – was proposed in 1985 [14]. Several types of this scanning near-field optical microscopy generally achieve label-free, non-destructive, and super-resolution imaging far below the diffraction limit. Tip-enhanced Raman spectroscopy combines scanning probe microscopy with surface-enhanced Raman spectroscopy and is very promising for nanoscale chemical analysis [15].

Low-temperature tip-enhanced Raman spectroscopy relies on nanofabricated plasmonic tips [16]. This method dramatically increases Raman scattering by the contribution of both electromagnetic and chemical amplification mechanisms, resulting in a very high sensitivity. The electromagnetic amplification is related to the localized surface plasmon excitation, while the chemical amplification is related to the local electronic structure of the sample and depends strongly on the excitation wavelength. We measured ultrathin zinc oxide films epitaxially grown on a surface of Ag(111) (**Fig. 5a**). The electronic resonance of the zinc oxide film varies depending on its thickness. The two-monolayer thick zinc oxide is on-resonance with an

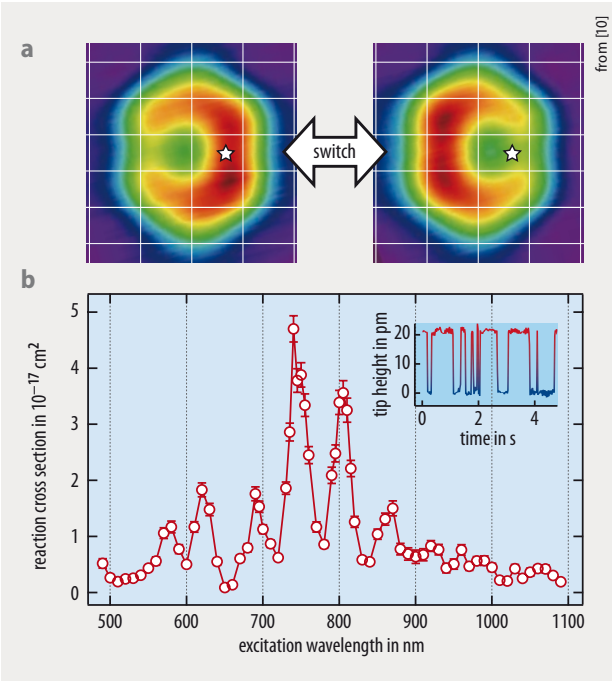

Fig. 4 Scanning tunneling microscope images prove the single-molecule tautomerization of porphycene (a). The near-field action spectrum obtained by the Au tip with a groove on the shaft (b) shows a modulation. The two-state random telegraph noise results from plasmon-driven single-molecule tautomerization (inset).

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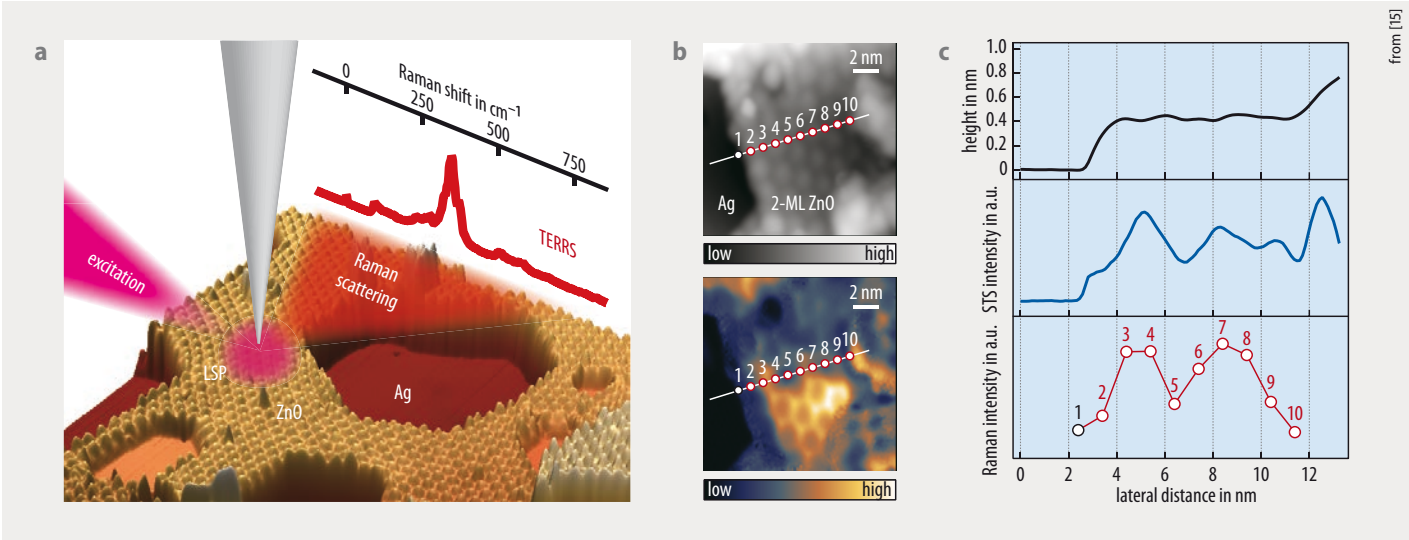

Fig. 5 The localized surface plasmon is excited at the apex of a sharp tip which generates a locally enhanced Raman scattering signal from ultrathin zinc oxide films epitaxially grown on a Ag(111) surface (a). A scanning tunneling microscope image (b, top) and a scanning tunneling spectroscopy mapping (bottom) show the boundary between the Ag surface and the ultrathin zinc oxide film. Height and intensities are measured at ten points using scanning tunneling microscopy (c, black), scanning tunneling spectroscopy (blue) and tip-enhanced resonance Raman spectroscopy (red).

excitation of 633 nm. An intense Raman signal is measured, which becomes weaker at 532 nm or 780 nm. The spatial resolution depends on the distance of tip and surface distance and reaches about one nanometer in the tunneling regime. One explanation is a strong-field confinement which results from the presence of an atomic-scale protrusion on the tip apex. The combination with scanning tunneling spectroscopy shows that the intensity of the tip-enhanced resonance Raman spectroscopy is correlated with the local electronic resonance of the interface between the zinc oxide and the Ag(111) surface (**Fig. 5b – f**). In addition, local phonon modes in the resonance Raman scattering and local electronic states are correlated at a nanometer resolution. Thus, tip-enhanced resonance Raman spectroscopy provides a new approach for the atomic-scale optical characterization of local electron-phonon coupling.

Perspective

The combination of low-temperature scanning tunnelling microscopy and plasmonics offers unique opportunities to study the interactions of nanolight and matter at the atomic and molecular level. Recently, light confinement reached the sub-nanometer scale for atomic-scale structures like protruding single atoms or atomic edges in facets in metallic nanostructures [17]. Low-temperature tip-enhanced Raman spectroscopy enables Raman imaging with Ångström-scale resolution [18]. This might allow for realizing atomic-scale optical spectroscopy in real-space and real-time. The interaction may also lead to new nanoscale optoelectronic devices with exceptional high sensitivity and efficiency [19].

References

[1] *L. Novotny* and *B. Hecht*, Principles of Nano-Optics, 2nd ed., Cambridge University Press, Cambridge (2012)
[2] *M. I. Stockman* et al., J. Opt. **20**, 043001 (2018)
[3] *H. Böckmann* et al., Nano Lett. **19**, 5725 (2019)
[4] *R. Berndt* and *J. K. Gimzewski*, Phys. Rev. B **48**, 4746 (1993)
[5] *S. Liu, M. Wolf* and *T. Kumagai*, Phys. Rev. Lett. **121**, 226802 (2018)
[6] *G. Binnig* et al., Phys. Rev. Lett. **55**, 991 (1985)
[7] *M. Wolf, E. Knoesel* and *T. Hertel*, Phys. Rev. B **54**, R5295 (1996)
[8] *U. Aslam* et al., Nat. Catal. **1**, 656 (2018)
[9] *S. Mukherjee* et al., Nano Lett. **13**, 240 (2012)
[10] *H. Böckmann* et al., Nano Lett. **18**, 152 (2018)
[11] *H. Böckmann* et al., J. Phys. Chem. Lett. **10**, 2068 (2019)
[12] *M. L. Brongersma* et al., Nat. Nanotechnol. **10**, 25 (2015)
[13] *A. M. Brown* et al., ACS Nano **10**, 957 (2016)
[14] *J. Wessel*, J. Opt. Soc. Am. B **2**, 1538 (1985)
[15] *A. B. Zrimsek* et al., Chem. Rev. **117**, 7583 (2017)
[16] *S. Liu* et al., Nano Lett. **19**, 5725 (2019)
[17] *J. Kern* et al., Nano Lett. **12**, 5504 (2012); *M. Urbieta* et al., ACS Nano **12**, 585 (2018); *F. Benz* et al., Science **354**, 726 (2016)
[18] *J. Lee* et al., Nature **568**, 78 (2019); *Y. Zhang* et al., Nat. Sci. Rev. **6**, 1169, (2019)
[19] *J. J. Baumberg* et al., Nat. Mater. **18**, 668 (2019)

The author

Takashi Kumagai received his PhD degree from Kyoto University, Japan, in 2011. Afterwards, he joined the Fritz-Haber Institute of the Max-Planck Society with a research fellowship awarded from the Japan Society for the Promotion of Science. In 2013, he was appointed a research group leader at Fritz-Haber Institute heading the Nanoscale Surface Chemistry Group. Since this year, he has been cross-appointed associate Professor at the Institute for Molecular Science, Japan, and started a new research group there. He has received several awards for early career scientists, including the Inoue Research Award for Young Scientists in 2013 (Japan), the Morino Award for Molecular Science in 2014 (Japan), the Gerhard Ertl Young Investigator Award in 2016 (Germany).

Dr. Takashi Kumagai, Fritz-Haber Institute of the Max-Planck Society and Institute for Molecular Science, Japan

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