Surface and Interface Science Laboratory (2021)
Chief Scientist: Yousoo Kim (Dr.Eng.)

(0) Research field

CPR Subcommittee**:** Chemistry

Keywords:

Scanning tunneling microscopy, Surface and Interface, Energy transfer and conversion, Single-molecule chemistry and spectroscopy

(1) Long-term goal of laboratory and research background

Our research aims at describing **the details of energy transport and conversion at solid surfaces and molecular interfaces in the nanoscale regime.** Excitation of molecules triggers various important energy conversion processes, such as luminescence, photochemical reactions, and photovoltaics. A detailed understanding of the molecular excited states is crucial to developing organic energy conversion devices based on opto-electronic/opto-chemical processes. We developed a scanning tunneling microscope (STM) combined with optical systems both for photon detection and for optical illumination to investigate energy transfer, conversion, and dissipation processes of various quantum states, such as spin, phonon, and exciton, confined in molecular interfaces from a single isolated molecule to well-ordered molecular assembles.

(2) Current research activities (FY2021) and plan (until Mar. 2025)
[Research activities in FY2021]

(A) Terahertz-field-driven scanning tunneling luminescence spectroscopy

We developed a novel microscopy technique that combines the ability to manipulate the motion of electrons on a femtosecond timescale and to detect a photon at sub-nanometer resolution [ACS Photonics 8 (2021) 982] (Fig.1). A lens was placed in such a way as to focus terahertz (THz) pulses onto the tip of the scanning tunneling microscope (STM). Photons produced from these pulses were then collected using a second lens and directed to a photon detector, allowing the desired investigation of the energy dynamics of quantum conversions that occur during STM ultrafast probing of materials at the atomic level. The THz-STM offers a new platform for us to conduct experiments involving sensing and controlling quantum systems, opening new doors for nanoscale science and the development of nanotechnologies.

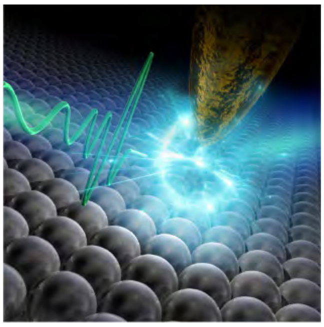

Figure 1. Ultrafast photon detection with a THz-STM

(B) Chemical identification and bond control of skeletons in a coupling reaction

We have generated the π-skeleton in a molecule, which governs carbon materials' electronic and optical properties, by on-surface synthesis and demonstrated chemical identification and control of the chemical bonding at the single chemical bond level [J. Am. Chem. Soc. 143 (2021) 9461] (Fig.2). The surface synthesis of the π-skeleton by deposition and heating of terminal alkyne molecules on a silver substrate surface, combined with STM, STS, and STM-TERS techniques, has enabled us to detect the electronic structure and local vibrational modes of the carbon skeleton at the single chemical bond level as well as to characterize its shape at the sub-molecular scale. The STM-TERS technique is a powerful tool for the detection and characterization of the electronic structure of carbon skeletons. This has revealed unknown carbon skeletons that could not be determined by conventional STM observation alone. The results of this research are expected to contribute to developing technologies for generating new carbon skeletons with atomic precision by surface synthesis and the associated development of new carbon materials.

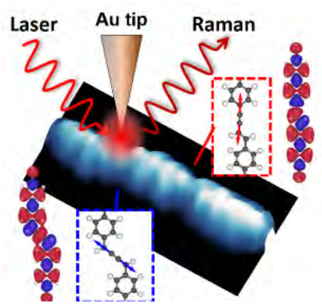

Figure 2. STM-TERS measurement of a single molecule

(C) Single-molecule laser nanospectroscopy with micro-electron volt energy resolution

We developed a new nanospectroscopy technique to measure a spectrum from a single molecule [Science 373 (2021) 95] (Fig. 3). The sensitivity of this method was demonstrated by taking two molecules that differed only slightly: at the center of one molecule, two hydrogen atoms each had an additional neutron. The single-molecule photoluminescence technique could detect this tiny mass difference between the molecules. This technique uses a laser beam to drive the electromagnetic field of a plasmon—electrons in a metal vibrating in concert—that forms between the tip of an STM and the metal substrate where the sample is located. Since the plasmon is a mere two nanometers in diameter—roughly 100 times smaller than the narrowest width of a focused laser beam—the technique's spatial resolution is very high, which allows us to reveal the nature of molecules with unprecedented precision.

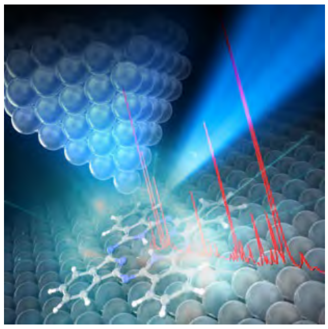

Figure 3. Single-molecule photoluminescence spectroscopy with high energy- and spatial-resolution

(D) Dissociation mechanism of a single O2 molecule chemisorbed on Ag(110)

We clarified how a molecule of oxygen (O2) on a silver surface separates into two oxygen atoms [J. Phys. Chem. Lett. 12 (2021) 9868] (Fig. 4). An STM tip was used to inject electrons into a single O2 molecule by applying positive voltage pulses, or to inject holes with negative voltage pulses. Both processes broke the oxygen–oxygen bond, resulting in two separate oxygen atoms on the surface. Two sequential excitations were needed to overcome the relatively high reaction barrier, and the molecules were excited to higher-order vibrational states before dissociating. The reaction pathway is an excitation from the ground state to higher excitations of the vibrational states, namely overtones; in our case, higher than the fifth excited state. Studying how the dissociation yield depends on the energy of electrons/holes sheds light on the excitation channels at work. This knowledge will help scientists to optimize industrially important reactions.

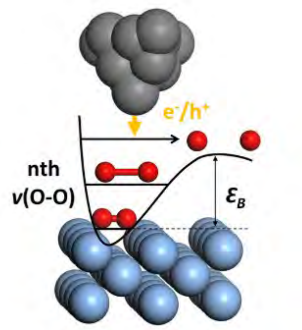

Figure 4. O-O bond dissociation by injecting tunneling electrons

[Future plan until Mar. 2025]

In addition to the fundamental technology of STM spectroscopy that we have accumulated so far, we will construct a spatio-temporal quantum dynamics platform that incorporates the high temporal resolution provided by ultrafast pulsed lasers, based on the results obtained through our recent fusion research with lasers. This will enable us to track and visualize the dynamic processes of spin, heat, and reactions with high spatio-temporal resolution.

(3) Current members (FY2021)

(Chief Scientist)
Yousoo Kim
(Senior Research Scientist)
Norihiko Hayazawa, Yasuyuki Yokota, Tohru Takarada, Masae Horinouchi
(Senior Scientist)
Hiroshi Imada
(Research Scientist)
Emiko Kazuma, Shunji Yamamoto, Seungran Lee, Reizo Kato
(Special Postdoctoral Researcher)
Rafael Buan Jaculbia, Chi Zhang, Qianchun Weng, Misun Hong, Kensuke Kimura, Raymond Wong
(Postdoctral Researcher)
Miyabi Imai
(Junior Research Associate)
Minhui Lee, Takuya Miyazaki, Yuzu Kobayashi
(International Program Associate)
Inhae Zoh, Jeongsuk Cheon
(Student Trainee)
Jaehyun Bae, Maki Torimoto, Kaito Kondo, Hiroki Sato, Yoto Fujita, Minoru Takeda, Ami Iwashima
(Technical Staff)
Yoshiko Shimizu, Hiroko Yoshino
(Part-time Worker)
Yuki Hasegawa
(Assistant)
Chikako Kuramochi, Yumi Kuramitsu

(4) Representative research achievements

1. "Terahertz-field-driven scanning tunneling luminescence spectroscopy", Kensuke Kimura, Yuta Morinaga, Hiroshi Imada, Ikufumi Katayama, Kanta Asakawa, Katsumasa Yoshioka, Yousoo Kim and Jun Takeda, **ACS Photonics 8** (2021) 982-987.

2. "Chemical identification and bond control of skeletons in a coupling reaction", Chi Zhang, Rafael B. Jaculbia, Yusuke Tanaka, Emiko Kazuma, Hiroshi Imada, Norihiko Hayazawa, Atsuya Muranaka, Masanobu Uchiyama and Yousoo Kim, **J. Am. Chem. Soc. 143** (2021) 9461-9467.

3. "Single-molecule laser nanospectroscopy with micro-electron volt energy resolution", Hiroshi Imada, Miyabi Imai-Imada, Kuniyuki Miwa, Hidemasa Yamane, Takeshi Iwasa, Yusuke Tanaka, Naoyuki Toriumi, Kensuke Kimura, Nobuhiko Yokoshi, Atsuya Muranaka, Masanobu Uchiyama, Tetsuya Taketsugu, Yuichiro K. Kato, Hajime Ishihara and Yousoo Kim, **Science 373** (2021) 95-98.

4. "Monatomic iodine dielectric layer for multimodal optical spectroscopy of dye molecules on metal surfaces", Yasuyuki Yokota, Raymond A. Wong, Misun Hong, Norihiko Hayazawa and Yousoo Kim , **J. Am. Chem. Soc. 143** (2021) 15205-15214.

5. "Localized graphitization on diamond surface as a manifestation of dopant"s, Francesca Celine I. Catalan, Le The Anh, Junepyo Oh, Emiko Kazuma, Norihiko Hayazawa, Norihito Ikemiya, Naoki Kamoshida, Yoshitaka Tateyama, Yasuaki Einaga and Yousoo Kim, **Adv. Mater. 27** (2021) 2103250, 1-9.

Supplementary

Group photo of Surface and Interface Science Laboratory

Laboratory Homepage

http://www.riken.jp/en/research/labs/chief/surf_interf/

http://www2.riken.jp/Kimlab/