Usage Report for Fiscal Year 2018

Project Title:

Theoretical study of interaction between tunneling electrons and individual molecules at surfaces

Name:

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1. Background and purpose of the project, relationship of the project with other projects

During the past decade, computer simulations based on a quantum mechanics have developed an increasingly important impact on solid-state physics and chemistry and on materials science. In field of material science, the surface chemistry is fundamentally important in many areas, such as molecular electronics, heterogeneous catalyst, fuel cell, etc. The adsorption of molecules onto a surface is a necessary prerequisite to any surface mediated chemical process. Understanding the bonding nature between the molecule and the surface on the basis of the electronic structure is therefore one of the most important issues in this field. The computational methods like density functional theory (DFT) have played a prominent role to elucidate the interaction between the molecule and the surface. Combination of DFT calculation and the method based on quantum many-body theory also provides a powerful approach to describe magnetism and dynamics on the surface with a high accuracy and efficiency. In addition, the computational method can be useful to study the details of energy transport and conversion among photon and electrons mediated with adsorbate at solid surfaces in the nanoscale regime. From the theoretical investigation of the adsorbed molecule on surface in combination with scanning tunneling microscopy and spectroscopy (STM/STS) experiment, we could expect the following research goals; 1) the deep understanding of the chemical/physical properties of an adsorbate on the surface not only in ground state but also in excited state, 2) the fine control of the chemistry on the surface. The overall purpose of our theoretical work is closely related with research goal - describing the details of energy transport and conversion at solid surfaces and interfaces in the nanoscale regime - of our laboratory, Surface and Interface Science laboratory.

2. Specific usage status of the system and calculation method

We have been studying the molecular adsorption on the well-defined metal surface using computational method in combination with experimental method. In our studies, first-principles simulations have been carried out using the Vienna Ab-initio Simulation Package (VASP) code and Quantum Espresso code in the density functional level of theory. The pure DFT methods have been mostly used and the inner electrons are replaced by projector augmented wave pseudopotentials (PAW). The climbing image nudged elastic band method (CI-NEB) is used to determine the transition states that are confirmed by imaginary frequency modes. In most of cases, STM image simulations are performed using Tersoff-Hamann approach. The computational results are compared with the available experimental result obtained from STM in our group. For the gas phase molecules, the Gaussian09 and Gaussian16 programs with atomic-orbital basis set are also effectively utilized to obtain stable geometries and corresponding electronic structures.

We also have been studying the many-body phenomena in molecular adsorption system, in particular the Kondo effect. The characteristic electronic state resulting from the Kondo effect, so-called Kondo singlet state appears as a sharp peak structure (Kondo peak) at the Fermi level (EF) in STS. In order to simulate the Kondo peak, we build numerical renormalization group (NRG) code and the STS simulation code based on the Keldysh Green's function method.

Electron-transport and luminescence properties of systems, that consist of a single molecule, substrate and the STM tip, are also our main research target. DFT calculations and the first-principles Green's function methods based on the many-body perturbation theory (MBPT) are used to investigate the basic properties of components, i.e., the adsorption nature of molecules and dielectric properties of the substrate as well as the excited electronic states of molecules with a high accuracy and efficiency. Based on the obtained results, we construct an effective model and investigate electron dynamics in transport and luminescence processes using the Keldysh Green's function method.

3. Result

(1) STM study combined with DFT calculations for photochemistry and plasmon chemistry on metal surfaces [E. Kazuma, J. Jung, H. Ueba, M. Trenary, and Y. Kim, Prog. Surf. Sci. 93, 163 (2018); E. Kazuma, J. Jung, H. Ueba, M. Trenary, and Y. Kim, Science 360, 521 (2018)]

We recently carried out STM study combined with DFT calculations to clarify the reaction mechanisms responsible for both photodissociation and the plasmon-induced dissociation of dimethyl disulfide, $(CH_3S)_2$, molecules adsorbed on Ag(111) and Cu(111) surfaces. Excitation mechanisms in photochemistry and in plasmon chemistry on metal surfaces (Fig. 1) are as follows: (i) direct intramolecular excitation, (ii) charge transfer (direct excitation) from bulk or surface states to unoccupied molecular orbitals, and (iii) indirect hot-electron transfer to the unoccupied molecular orbitals.

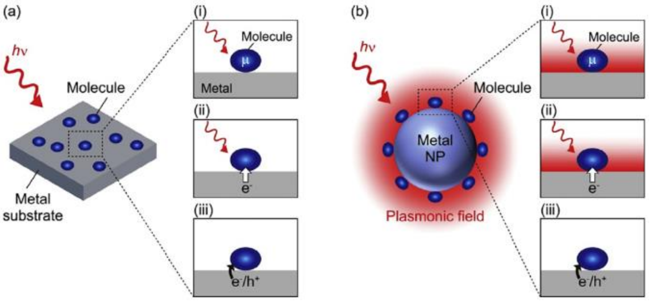

Fig. 1. Excitation mechanisms in (a) photochemistry on a metal substrate and (b) plasmon chemistry on a metal nanoparticle (NP).

The combination of optical excitation and detection with the STM has been applied to local spectroscopies such as STM-induced luminescence and STM tip-enhanced Raman scattering. In particular, the STM combined with optical excitation has been also applied to investigation of photon-induced molecular motions and dynamics or chemical reactions such as photoisomerization and plasmon-induced chemical reactions (Fig. 2).

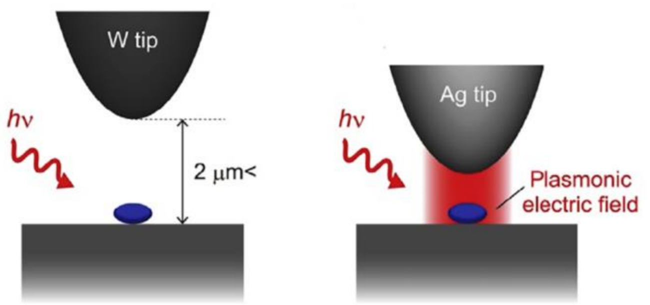

Fig. 2. Schematic illustrations of experiments using an STM for photochemical reactions and plasmon-induced chemical reactions

The real-space investigation using the STM revealed that photodissociation of the S–S bond in (CH$_3$S)$_2$ molecules adsorbed on Ag(111) and Cu(111) surfaces was induced by visible-light irradiation (Fig. 3). After light irradiation without the influence of the STM tip, some of the ellipsoids had broken into two identical ball-shaped protrusions, implying the formation of two CH$_3$S molecules due to the dissociation of the S–S bond. Any other molecular motion such as rotation, translation and desorption, was not observed. Only the molecular photodissociation occurs randomly within the light spot.

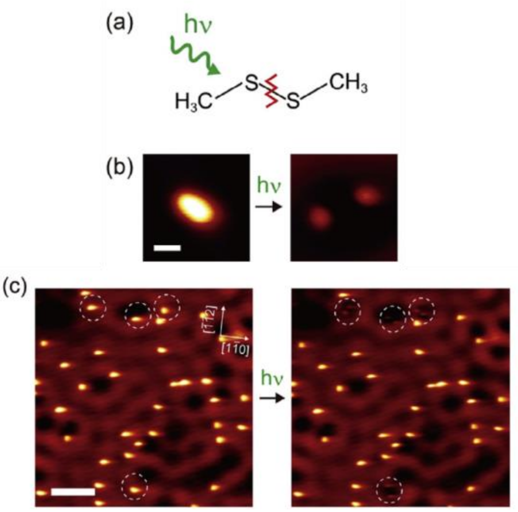

Fig. 3. (a) Structure of a (CH$_3$S)$_2$ molecule, indicating the dissociation of the S–S bond by photons. (b, c) Topographic STM images of (CH$_3$S)$_2$ molecules adsorbed on Ag(111) before and after irradiation with 532 nm light.

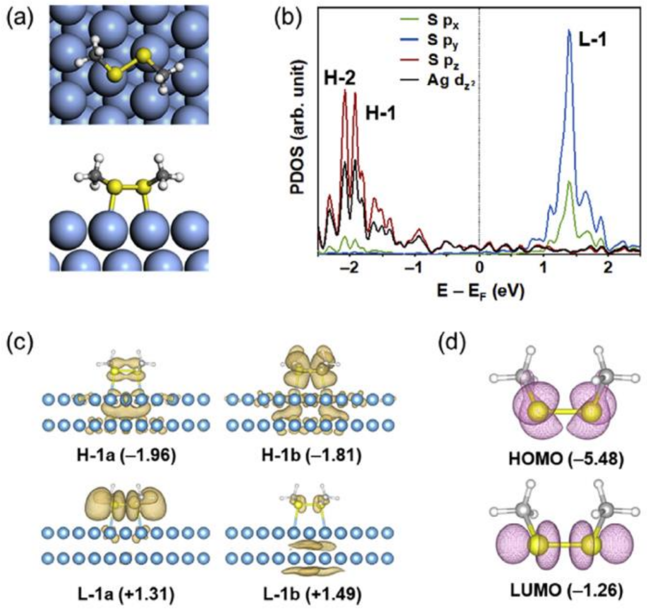

Fig. 4. (a) The adsorption structures of a (CH$_3$S)$_2$ molecule on Ag(111) optimized by DFT calculations. (b) The projected DOS of three p-states on S atoms in a (CH$_3$S)$_2$ molecule and d_{z^2}-state of two metal atoms that are underneath the S atoms and directly interact with the molecule on Ag(111). (c) The spatial distribution of molecular frontier states nearest to E_F for an isolated (CH$_3$S)$_2$ molecule on Ag(111). (d) The spatial distribution of the HOMO and LUMO orbitals in the gas phase (CH$_3$S)$_2$.

To elucidate the photodissociation mechanism of (CH$_3$S)$_2$ molecules on the Ag(111) and Cu(111) surfaces, we carried out periodic DFT calculations. The atomically resolved STM images reveal the adsorption site of the molecules: the molecular center is positioned above bridge sites, and two S atoms are located at the on-top sites of adjacent metal atoms (Fig. 4a). The local density of states (LDOS) of an (CH$_3$S)$_2$ molecule and the projected density of states (PDOS) of the three p-states of its two S atoms calculated on the metal surfaces indicate that the S p-states mainly contribute to the first prominent LDOS peaks of (CH$_3$S)$_2$ nearest E_F. The occupied and unoccupied molecular states near the E_F are dominantly composed of the S p_z-state, and S p_x- and p_y-states, respectively (Fig. 4b). The spatial distributions of molecular frontier states for (CH$_3$S)$_2$ adsorbed on the Ag(111) surfaces indicate that H-1 state (~-1.9 eV) consist of π-bonding orbital along the S-S bond (π_{SS}) and nonbonding lone-pair type orbitals on the S atoms (n_S), and L-1 state (~ +1.4 eV) is characterized by the antibonding orbital localized on the S–S bond (σ^*_{SS}) (Fig. 4c). The H-1b and L-1 states are very similar to the HOMO and LUMO states of $(CH_3S)_2$ in the gas phase, respectively (Fig. 4d). The appearance of H-1a state in the frontier region can be understood by enhancement of molecular planarity due to the adsorption on the surface, where the dihedral angle of 82.8° along the S-S bond in the gas phase increases to 134.2° (126.7°) on Ag (Cu) surface. The spatial distributions of electronic states on Cu(111) are almost identical to those of the electronic states observed on Ag(111). In the gas-phase reaction, dissociation of the S–S bond of $(CH_3S)_2$ predominantly occurs with 248 nm (~5.0 eV) light through the direct electronic excitation from nS to σ^*_{SS}. Considering the remarkable similarity of the frontier states on the metal substrates to the molecular orbitals of the gas phase $(CH_3S)_2$ (Fig. 4c and 4d), the photodissociation of the S–S bond on the metal surface can also occur through direct electronic excitation between the frontier electronic states ($n_S \rightarrow \sigma^*_{SS}$). The computationally estimated energy gaps for the excitation pathway ($n_S \rightarrow \sigma^*_{SS}$) are 3.12-3.30 eV (376-397 nm) and 2.27-2.51 eV (494 - 546 nm) on Ag(111) and on Cu(111), respectively. Although the conventional DFT calculations cannot exactly describe the HOMO-LUMO gap due to the limitations of neglecting exact Hartree-Fock exchange, the computational results not only describe the reduction of the energy gap from the HOMO–LUMO gap of gas phase $(CH_3S)_2$ but also provide a way to qualitatively explain the experimental results in which the threshold energy for photodissociation on Cu(111) was found to be lower than that on Ag(111). Moreover, the reduced energy gap due to hybridization, i.e., coupling between the electronic states of adsorbate and metal substrate, enables photodissociation by visible light. The alignment of molecular frontier states with respect to the metal-states of the two metal atoms underneath the S atoms reveals the degree of interfacial hybridization between molecular orbitals and metal states, for which the energy region corresponds to the edge of Ag 4d state. Fig. 4b shows that the HOMO-derived states align well with the d_{z^2}-state of the two Ag atoms underneath the S atoms, but there is no significant distribution of the metal-state in the unoccupied region. The same tendency was also observed on the Cu(111) surface. The spatial distribution of molecular orbitals for $(CH_3S)_2$ adsorbed on the metal clearly represents the strong and weak interfacial hybridization between the molecule and the metal at HOMO- and LUMO-derived states, respectively (Fig. 4c). In particular, the weakly hybridized electronic structure in the unoccupied region may suppress the rapid relaxation of the excited states. We thus conclude that the weak interactions between the frontier molecular orbitals and the metal states, especially in the unoccupied region, extend the excited-state lifetimes sufficiently to induce photodissociation. The experimentally observed photodissociation by visible light can be explained by reduction of the optical energy gap of $(CH_3S)_2$ due to the hybridization between electronic states of adsorbate and metal substrate, in which the molecular frontier states with less overlap with the metal substrate enables a reaction pathway for the photodissociation of adsorbate.

The STM also allows real-space analyses of the plasmon-induced chemical reaction as abovementioned. In addition, the reaction time of a single molecule is provided by the current trace measurement, which gives insights into the elementary reaction pathways that cannot be accessed by conventional spectroscopies and the analysis of the wavelength dependence of the yield. Fig. 5a shows an experimental scheme of the current trace when the STM tip was positioned over the $(CH_3S)_2$ molecule on Ag(111) under light irradiation. A one-time change in tunneling current indicates that one kind of molecular motion or reaction happened. In the case of the $(CH_3S)_2$ molecule, a sudden drop in the current was caused by the dissociation of the molecule (Fig. 5b).

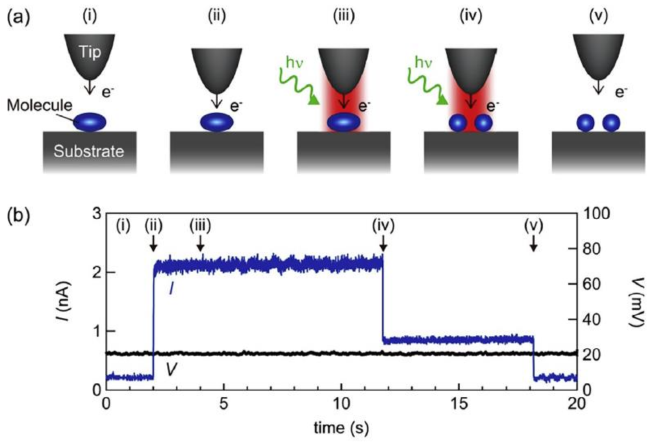

Fig. 5. (a) Schematic illustration of the current trace experiment for the plasmon-induced single molecule reaction. (b) Current trace for detecting the dissociation event for the single $(CH_3S)_2$ molecule on Ag(111) induced by the plasmon excited with p-polarized light at 532 nm.

The STM can also reveal the reaction pathways initiated from the TNI states formed by electron transfer from the metal to the molecule via the IET process. Both the hot electrons of the plasmon and the tunneling electrons inelastically transfer to the unoccupied molecular orbitals to form the TNI states. The reaction pathways initiated from the TNI states in the same energy regions should be the same regardless of the origin of the excitation source, because both the hot electrons and tunneling electrons had a broad energy distribution from E_F to the energy of the plasmon (E_F+E_{LSP}) and the applied sample bias voltage (E_F+eV_{bias}), respectively. Our current trace measured for the single-molecule reaction induced by the plasmon exhibited only a one-time change due to dissociation and is not accompanied by rotational motion prior to dissociation. This excluded the hot-electron-mediated process as an elementary pathway for the plasmon-induced dissociation of $(CH_3S)_2$. By considering the results of the wavelength dependence of dissociation yield and the DFT calculations, we concluded that the plasmon-induced dissociation of $(CH_3S)_2$ occurred through the direct dissociation pathway from neutral excited states generated by direct intramolecular excitation (Fig. 6).

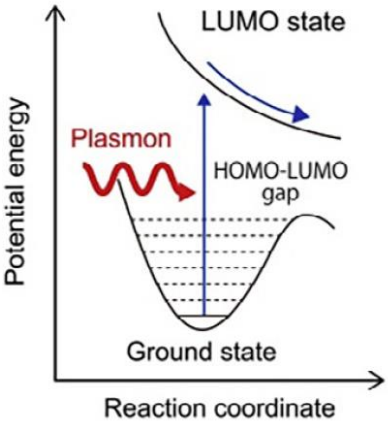

Fig. 6. Schematic illustrations of the potential energy surfaces (PES) for direct excitation mechanism for plasmon-induced chemical reaction.

(2) Electron-phonon coupling at surface and interfaces ["Inelastic electron tunneling spectroscopy by STM of phonons at solid surfaces and interfaces" E. Minamitani, N. Takagi, R. Arafune, T. Frederiksen, T. Komeda, H. Ueba, Prog. Surf. Sci., 93, 131, (2018)]

Surfaces provides unique platforms to investigate the basic aspects of phonons by means of various spectroscopic techniques. Most surface-phonon spectroscopies correlate their signal with the energy-loss process during incident particle or photon scattering. Representative methods are high-resolution electron energy loss spectroscopy (HREELS), helium atom scattering (HAS) and Raman scattering. Surface phonons have been intensively measured by these techniques, and much knowledge has been accumulated. The measured spectra typically provide ensemble averages over macroscopic sample areas. Currently, surface-phonon spectroscopy with atomic-scale resolution is in high demand. Revealing the correlation of lattice dynamical properties with local geometric and electronic structures at clean, reconstructed and molecule-adsorbed surfaces would lead to a deeper understanding of phonon-related phenomena and possibly to tailoring of the functionalities of surface nanostructures. The recent boost in research on atom-layered materials such as graphene, X-enes (X = Si, Ge, Sn, and so on), and transition metal dichalcogenides (TMDCs) makes it highly desirable to acquire insights on the microscopic relations of their electronic and optical properties with the surface and local phonons.

Scanning tunneling microscopy (STM) enables the observation of surface structure and electronic states with atomic-scale spatial resolution. With the advent of low-temperature, ultra-high vacuum STM equipment and inelastic tunneling electron spectroscopy (IETS), the energy loss of tunneling electrons through vibration excitations has become measurable at a single-atom/molecule level. Although STM-IETS studies have been performed intensively for single molecules, there are only few reports on the application of STM-IETS to surface and interfacial phonons. Revealing the inelastic signals from these should open up a new avenue of STM-IETS to study phonon-related solid-state physics.

In this research project, we develop theoretical formalism on phonon excitation with STM-IETS for solid surfaces and interfaces. We summarized our theoretical methods and application on STM-IETS measurement on surface phonon on Cu(1 1 0) and localized phonons at the interface in between graphene and SiC.

(3) Raman spectra of self-assembled monolayers on gold electrode

We are developing new experimental technique, tip-enhanced Raman spectroscopy (TERS) in liquid environment, to achieve nanoscale Raman signal mapping of organic molecules on metal electrodes with local structural properties. While a gold tip enhances the incident electric filed as much as 100, TERS measurements still reacquire the highly Raman active molecules to be studied because the long accumulation of the Raman signal is hampered by instrumental instability. It is thus prerequisite to systematically study the Raman intensity as well as the vibrational energy for the various kinds of organic molecules (self-assembled monolayers (SAMs) on gold electrode). In this study, we have succeeded in obtaining Raman spectra of benzenethiol (PhSH) adsorbed on gold clusters (Fig. 7(a)). We found that the simple gold dimer model is enough to reproduce the experimental Raman spectrum (Fig. 7(b)).

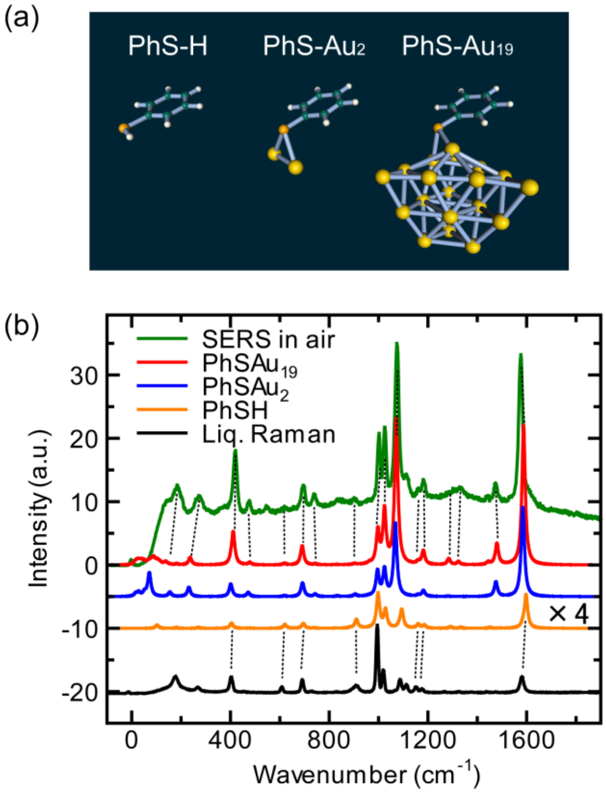

Fig. 7 (a) Molecules calculated in this study. (b) Experimental and calculated Raman spectra of PhSH SAM.

(4) Single molecule electroluminescence induced by the metal-molecule charge transfer [K. Miwa, H. Imada, M. Imai-Imada, K. Kimura, M. Galperin, and Y. Kim, Nano Letters in press (2019)]

Transport and optical properties of a single molecule attached to conductive materials have attracted much attention owing to their scientific importance and potential applications in single molecule devices. With a recent progress of experimental techniques, investigation of the single molecule properties at sub-nanometer spatial resolution have been achieved by the use of scanning tunneling microscope (STM)-induced light emission, where the tunneling current of STM is utilized as an atomic-scale source for induction of light emission from a single molecule. Despite the extensive experimental studies, the microscopic mechanism in the STM-induced light emission (STM-LE) from a single molecule has yet to be clarified. In this study, we formulate single molecule electroluminescence driven by electron transfer between molecule and metal electrodes with the basis of a many-body state representation of the molecule. The effects of Coulomb interaction between electrons occupying molecular orbitals on both conductance and luminescence spectra are investigated by means of the nonequilibrium Hubbard Green's function technique combining with first principles calculations.

We analyzed STM-Le from a single phthalocyanine molecule adsorbed on a trilayer of NaCl films grown on a Ag(111) surface, which was recently investigated in the experiments. We found that the intra-molecular Coulomb interactions are key factors in reproducing both the experimentally observed conductance and luminescence spectra: The Coulomb blockade, that arises from the Coulomb interaction of an electron in highest occupied molecular orbital (HOMO) with an electron tunneling to higher-energy molecular orbitals from the metal electronic state, affects the electron dynamics underlying the single molecule electroluminescence and electron transport through the single molecule. The excitonic effects owing to intra-molecular Coulomb interaction Can be seen in the experimental data prominently. Moreover, the mechanism of the current driven single molecule electroluminescence is interpreted in the viewpoint of the transition between many-body states of the molecule, and is verified by comparison between computational and experimental results. Thus, we concluded that the constructed theory provides a unified description of both transport and optical properties of single molecules in the nanometer-scale junction, and it would contribute to a fundamental understanding of optoelectronic conversion in single molecule junctions.

4. Conclusion

We have tried to examine a variety of molecular behaviors on the surface in FY2018. Our theoretical studies combined with experiments in FY2018 provide deep insight into a variety of chemical and physical phenomena on solid surface: (1) Photochemistry and plasmon-induced chemical reactions, (2) Electron-phonon coupling at surface and interfaces, (3) Raman spectra of self-assembled monolayers on gold electrode, (4) Single molecule electroluminescence induced by the metal-molecule charge transfer. We expect that our results can provide new perspective to develop a potential strategy for controlling electronic properties of molecular adsorbates on the surface.

5. Schedule and prospect for the future

(1) Controlling chemical reactivity of ultrathin oxide film

Ultrathin oxide film grown on metal substrate has been a subject of great interest not only as a supporting material for chemically active nanoparticles but also as a catalyst in the field of heterogeneous catalysis, where it provides various ways to control the properties of adsorbates via following factors: (i) charge transfer between adsorbates and oxide-metal interface, which is closely correlated with the electronic affinity (EA) of adsorbate and workfunction reduction, (ii) adhesion between oxide and metal layers with strong polaronic distortion, (iii) film thickness, and (iv) the chemical composition of oxide surface. Therefore, we will continue our work to find the way for controlling the chemical reactivity using theoretical and experimental studies. In FY2019, we will extend our study into dissociation of CH_3OH and O_2 on MgO/Ag(100) using combined STM and DFT methodology, in which the role of single atom catalyst implemented in oxide film will also be considered. In addition, the influence from solvent medium on the chemical reactions occurring on surface will be studied in order to provide insights into the electrochemical reactions. In particular, regarding the CH_3OH dissociation on MgO/Ag(100), we will try to find a way to selectively dissociate a bond in CH3OH, e.g., C-H, O-H, and C-O, using an ionic species on MgO film surface which is introduced through charge transfer between the oxide surface and oxide-metal interface. For the for O_2 dissociation on MgO/Ag(100), we should consider an influence from the charge redistribution between the oxide-metal interface and the adsorbate, because of O_2 has much higher EA than that of H_2O molecule. The other branch of our study is exploring the single atom catalyst on ultrathin oxide film, which is now widely studied due to its prominent importance in heterogeneous catalyst. Therefore, we will introduce single atom catalyst to oxide film and will study how to control its catalytic activity and selectivity. In addition, we are extending our model system to other ultrathin oxide film systems, such as titania and ceria. We believe that our study provides not only profound insight into the chemical reactivity control of ultrathin oxide film but also an impetus for investigating ultrathin oxide films for a wider range of applications.

(2) Molecular adsorption on solid surface: From single molecule to molecular network, and their optical properties

The controllable fabrication of molecular architectures is a topic of great importance not only as a fundamental subject in surface science but also for realizing molecular-scale electronic devices. Computational techniques can provide the underlying mechanisms for the formation of various molecular architectures experimentally observed by STM as well as single molecule adsorption. For the adsorption of single molecules on metal substrate, we suggested the origin of adsorption-induced stability reversal of photochromic DAE on metal surfaces and revealed that the interfacial orbital interaction originated from the weak electronic coupling between the molecular π-state and the electronic states of the Au surface can play a decisive role in constraining adsorption geometry even in the archetypal vdW adsorption system. For one-dimensional (1-D) systems, we have explained (i) the formation mechanism of 1D zipper-type architecture of azobenzene derivatives with the balanced non-bonding interactions, H-bonding and vdW interactions, between adjacent molecules and (ii) the dispersive electronic feature due to the π-orbitals stacking in 1-D molecular lines fabricated on the Si(001)-(2×1)-H. For 2D systems, we contributed to unveil the adsorption geometry of 2D molecular films composed of fluorinated fullerene

($C_{60}F_{36}$), which is strongly related to the distribution of frontier molecular orbitals and thus the n-type character of molecular film. In addition, we recently revealed that the interfacial electronic structure of individual adsorbate on solid surface is closely related to the chemical reactivity through the excitation with photon and plasmon. Our results provide not only deeper insight into the molecular adsorption process, but also a general basis for designing the architectures of molecular electronics with desired electronic properties. In FY2019, we will continue the research not only for a variety of molecular assemblies but also isolated molecule on the surfaces as follows: (i) the formation mechanism of van der Waals interface between π-conjugated molecule and novel metal substrate, and (ii) optical property of adsorbate on solid surface.

(3) Electronic structures of layered materials, such as graphene and dichalcogenide, and of framework materials, such as MOF and COF

Functionalization of layered materials, such as graphene and dichalcogenide, has attracted great scientific interest not only in controlling their physical properties but also in improving chemical adaptability to integrate them as a building block into a variety of functional devices. In particular, we first suggested that the atomic oxidation of graphene grown on a metal substrate results in the formation of graphene enolate, i.e., negatively charged oxygen adsorbed at ontop position on its basal plane, which is strikingly different from the formation of epoxy groups, i.e., adsorption of atomic oxygen at bridge position, on pristine graphene and on graphite. Whereas the enolate is the transition state between two nearest epoxides both on graphene and on graphite, we revealed that improved interfacial interaction between graphene and metal substrate during atomic oxidation plays a crucial role not only in the formation of graphene enolate as a local minimum but also in stabilizing it over the graphene epoxide. In addition, we recently studied the growth mechanism of covalent organic framework (COF) through photo-excitation. In FY2019, we are going to theoretically investigate (1) our very recent experimental finding of well-ordered graphene functionalization, in which the formation of graphene enolate would be one of the main driving forces, and (2) the catalytic effect of metal-organic framework (MOF).

(4) Magnetism of nanostructure on solid surface

Controlling the perpendicular magnetic anisotropy (PMA) at the surface/interface of ferromagnetic metals is the heart of modern magnetic devices based on the magnetic tunnel junctions. The electronic state at the surface/interface plays an important role to determine the interfacial PMA. In the field of surface science, it is well known that the electronic state at metal surface is drastically changed by molecular adsorption, which is also expected to affect PMA. We start ab-initio analysis of the PMA in an Fe(001) surface covered by Co-phthalocyanine (CoPc) molecule. As a preliminary results, we found that the PMA is enhanced up to 18% by CoPc adsorption, which is in good agreement with experimental results. We will continue further analysis on the origin of the above phenomena.

(5) Efficient ab-initio simulation of phonon properties in combination with machine learning technique

The evaluation of thermal properties based on the microscopic view is highly demanded to improve the thermal management in semiconducting devices. The dominant carrier in semiconducting material is phonons. Comparing to the electronic structure calculation, the computational cost for phonon related properties, such as phonon dispersion and electron-phonon coupling is much larger. To overcome this difficulty, we challenge to develop simulation method which combine ab-initio calculation and machine learning technique such as high-dimensional neural network potential.

(6) Raman spectra of self-assembled monolayers on gold electrode

As mentioned in the above section, we have established the simulation method of Raman spectra for organic monolayers of metal surfaces. We will try to perform experiments for next half year, and will perform DFT calculation to find next more attractive targets.

(7) Photoelectric conversion in single molecule on surface

Our studies on carrier dynamics in energy conversion processes are extended to the research on photoelectric conversion in single molecule. Single molecule luminescence can be induced by the tunneling current of STM, enabling us to investigate the electroluminescence processes of a molecule with submolecular spatial resolution in a well-defined manner. Especially, we focus on electron correlations in electroluminescence processes, e.g., charging of the molecule, formation of single/triplet excitons, radiative and nonradiative decay, and so forth. The key factor in the theoretical analysis is the calculation of (i) excited electronic states of the molecule as well as (ii) nonequilibrium electron dynamics in electroluminescence processes under applied bias. We plan to investigate these points using the method based on first-principles calculations and the nonequilibrium Green's function (NEGF) methods. Our study would make a contribution for understanding the fundamental nature of molecular electroluminescence and in the designing of novel functional materials for organic (opto)electronic devices.

Usage Report for Fiscal Year 2018

Fiscal Year 2018 List of Publications Resulting from the Use of the supercomputer

[Paper accepted by a journal]

1. Emiko Kazuma, Jaehoon Jung, Hiromu Ueba, Michael Trenary, and Yousoo Kim, "Real-space and real-time observation of a plasmon-induced chemical reaction of a single molecule", *Science* 360, 521 (May, 2018)

2. Emiko Kazuma, Jaehoon Jung, Hiromu Ueba, Michael Trenary, and Yousoo Kim, "STM studies of photochemistry and plasmon chemistry on metal surfaces", *Prog. Surf. Sci.* 93, 146 (December, 2018)

3. Emi Minamitani, Noriaki Takagi, Ryuichi Arafune, Thomas Frederiksen, Tadahiro Komeda, and Hiromu Ueba, "Inelastic electron tunneling spectroscopy by STM of phonons at solid surfaces and interfaces", Prog. Surf. Sci., 93, 131 (December 2018)

4. Kuniyuki Miwa, Hiroshi Imada, Miyabi Imai-Imada, Kensuke Kimura, Michael Galperin, and Yousoo Kim, "Many-Body State Description of Single-Molecule Electroluminescence Driven by a Scanning Tunneling Microscope", Nano Letters in press (2019) [DOI: 10.1021/acs.nanolett.8b04484]

[Oral presentation]

1. Y. Kim, "Real-space Observation of Energy Transfer between Two Molecules by Single-molecule Emission/Absorption Spectroscopy with an STM", IMPRS (International Max Planck Research School) Workshop 2018: From Models to Reality, Tegernsee, Germany, Feb. (2018)

2. K. Miwa, H. Imada, F. Chen, K. Kimura, M. Imai-Imada, Y. Kim, and M. Galperin, "Theory of current fluctuation for single molecule junction with intra-molecule Coulomb interaction and multimode vibronic interactions", American Physical Society March Meetings, California, USA, Mar. (2018)

3. K. Kimura, H. Imada, K. Miwa, M. Imai-Imada, S. Kawahara, J. Takeya, M. Kawai, Y. Kim, "Investigation of the Exciton Formation in a Single Molecule with a Scanning Tunneling Microscope", American Physical Society March Meetings, California, USA, Mar. (2018)

4. Y. Kim, "Energy conversion and transfer at a single molecule", 2018 KPS (Korean Physical Society) Spring Meeting, Daejeon, Korea, Apr. (2018)

5. Y. Kim, "STM investigation of energy conversion and transfer at a single molecule", France-Japan workshop on optoelectronics & Photonics, Paris, France, May (2018)

6. H. Imada, K. Miwa, M. Imai-Imada, S. Kawahara, K. Kimura, and Y. Kim, "Atomically-precise investigation of intermolecular energy transfer with scanning tunneling microscopy", The 12th International Conference on Excitonic and Photonic Processes in Condensed Matter and Nano Materials (EXCON 2018), Nara, Japan, Jul. (2018).

7. Y. Kim, “Single-molecule chemistry and spectroscopy with localized surface plasmon”, 14th International Conference on Atomically Controlled Surfaces, Interfaces and Nanostructures (ACSIN-14) & 26th International Colloquium on Scanning Probe Microscopy (ICSPM26), Sendai, Japan, Oct. (2018)

8. H. Imada, K. Miwa, M. Imai-Imada, K. Kimura, and Y. Kim, “Single-molecule absorption spectroscopy with STM”, 14th International Conference on Atomically Controlled Surfaces, Interfaces and Nanostructures (ACSIN-14)＆26th International Colloquium on Scanning Probe Microscopy (ICSPM26), Sendai, Japan, Oct. (2018).

9. R. A. Wong, Y. Yokota, M. Wakisaka, J. Inukai, and Y. Kim, “Electrochemically-driven charge transfer in redox-active self assembled monolayers: probing the electronic and structural changes”, 14th International Conference on Atomically Controlled Surfaces, Interfaces and Nanostructures (ACSIN-14) ＆26th International Colloquium on Scanning Probe Microscopy (ICSPM26), Sendai, Japan, Oct. (2018).

10. Y. Yokota, “Developments of In Situ and Ex Situ Techniques for Microscopic Studies of Electrochemical Reactions at Aqueous Solution/Electro Interfaces”, IMS symposium "Water at interfaces 2018", Okazaki, Japan, Jan. (2019).

[Poster presentation]

1. F. C. I. Catalan, N. Hayazawa, Y. Yokota, R. A. Wong, T. Watanabe, Y. Einaga, and Y. Kim, “Grain-Orientation Dependence of Anodic Corrosion Effects in Boron-Doped Diamond”, 12th New Diamond and Nano Carbons Conference (NDNC 2018), Arizona, USA, May (2018)

2. M. H. Balgos, E. A. Prieto, R. Jaculbia, E. Estacio, A. Salvador, Y. Kim, N. Hayazawa, and A. Somintac, “Low temperature scanning tunneling microscopy and spectroscopy of undoped LT-GaAs”, 36th SPP Physics Conference, Puerto Princesa, the Pilippines, Jun. (2018)

3. K. Kimura, H. Imada, K. Miwa, M. Imai-Imada, S. Kawahara, J. Takeya, M. Kawai, and Y. Kim, “Single-molecule investigation of a triplet exciton formation with a scanning tunneling microscope”, The 12th International Conference on Excitonic and Photonic Processes in Condensed Matter and Nano Materials (EXCON 2018), Nara, Japan, Jul. (2018).

4. M. Imai-Imada, H. Imada, K. Miwa, K. Kimura, J. Takeya, and Y. Kim, “Enhancement of single molecule electroluminescence by controlling excitation and deexcitation pathways”, The 12th International Conference on Excitonic and Photonic Processes in Condensed Matter and Nano Materials (EXCON 2018), Nara, Japan, Jul. (2018).

5. F. C. I. Catalan, N. Hayazawa, Y. Yokota, R. A. Wong, T. Watanabe, Y. Einaga, and Y. Kim, “Grain-orientation dependence of anodic corrosion in boron-doped diamond”, 14th International Conference on Atomically Controlled Surfaces, Interfaces and Nanostructures (ACSIN-14) & 26th International Colloquium on Scanning Probe Microscopy (ICSPM26), Sendai, Japan, Oct. (2018).

6. C. Zhang, E. Kazuma, and Y. Kim, "Surface-mediated stepwise evolution of chiral organometallic networks", 14th International Conference on Atomically Controlled Surfaces, Interfaces and Nanostructures (ACSIN-14)＆26th International Colloquium on Scanning Probe Microscopy (ICSPM26), Sendai, Japan, Oct. (2018).

7. M. Lee, H. Lim, J. Jung, and Y. Kim, "Highly-ordered hydroxylated graphene epitaxially grown on Cu(111)", 14th International Conference on Atomically Controlled Surfaces, Interfaces and Nanostructures (ACSIN-14)＆26th International Colloquium on Scanning Probe Microscopy (ICSPM26), Sendai, Japan, Oct. (2018).

8. M. H. M. Balgos, E. A. P. Prieto, R. B. Jaculbia, A. A. Salvador, E. S. Estacio, A. S. Somintac, N. Hayazawa, and Y. Kim, "Low temperature scanning tunneling microscopy and spectroscopy of undoped LT-GaAs", 14th International Conference on Atomically Controlled Surfaces, Interfaces and Nanostructures (ACSIN-14)＆26th International Colloquium on Scanning Probe Microscopy (ICSPM26), Sendai, Japan, Oct. (2018).

9. R. B. Jaculbia, K. Miwa, H. Imada, and Y. Kim, "Investigation of the adsorption structure of CuPc on NaCl/Ag(111) using STM", 14th International Conference on Atomically Controlled Surfaces, Interfaces and Nanostructures (ACSIN-14)＆26th International Colloquium on Scanning Probe Microscopy (ICSPM26), Sendai, Japan, Oct. (2018).

10. K. Kimura, H. Imada, K. Miwa, M. Imai-Imada, S. Kawahara, J. Takeya, M. Kawai, and Y. Kim, "Investigation of exciton formation mechanism in a single PTCDA molecule using a scanning tunneling microscope", 14th International Conference on Atomically Controlled Surfaces, Interfaces and Nanostructures (ACSIN-14)＆26th International Colloquium on Scanning Probe Microscopy (ICSPM26), Sendai, Japan, Oct. (2018).

11. Y. Yokota, N. Hayazawa, B. Yang, E. Kazuma, F. C. I. Catalan, and Y. Kim, "Vibrational analysis of aromaticthiol self-assembled monolayer on Au(111) using electrochemical STM-based tip-enhanced Raman spectroscopy", 14th International Conference on Atomically Controlled Surfaces, Interfaces and Nanostructures (ACSIN-14)＆26th International Colloquium on Scanning Probe Microscopy (ICSPM26), Sendai, Japan, Oct. (2018).

12. M. Hong, Y. Yokota, and Y. Kim, "Investigation of redox viologen systems at Au(111) interface using ex situ XPS", 14th International Conference on Atomically Controlled Surfaces, Interfaces and Nanostructures (ACSIN-14)＆26th International Colloquium on Scanning Probe Microscopy (ICSPM26), Sendai, Japan, Oct. (2018).

13. E. Kazuma, J. Jung, H. Ueba, M. Trenary, and Y. Kim, "STM investigations of plasmon-induced chemical reaction of dimethyl disulfide on metal surfaces", 14th International Conference on Atomically Controlled Surfaces, Interfaces and Nanostructures (ACSIN-14)＆26th International Colloquium on Scanning Probe

Microscopy (ICSPM26), Sendai, Japan, Oct. (2018).

14. M. Imada-Imai, H. Imada, K. Miwa, T. Shimizu, J. Jung, M. Kawai, and Y. Kim, “Energy-level alignment of a single molecule on the ultrathin insulating films with various thicknesses”, 14th International Conference on Atomically Controlled Surfaces, Interfaces and Nanostructures (ACSIN-14) & 26th International Colloquium on Scanning Probe Microscopy (ICSPM26), Sendai, Japan, Oct. (2018).

15. S. Chaunchaiyakul, H. Imada, E. Kazuma, F. Ishiwari, T. Fukushima, and Y. Kim, “A robust insulating molecular thin film”, 14th International Conference on Atomically Controlled Surfaces, Interfaces and Nanostructures (ACSIN-14)＆26th International Colloquium on Scanning Probe Microscopy (ICSPM26), Sendai, Japan, Oct. (2018).

16. M. Hong, Y, Yokota, and Y. Kim, “Spectroelectrochemical Investigation of Viologen at Graphite Interface Using Ex Situ XPS”, IMS symposium "Water at interfaces 2018", Okazaki, Japan, Jan. (2019).

17. R. A. Wong, Y, Yokota, M. Wakisaka, J. Inukai, and Y. Kim, “Redox-Dependent Electric Double Layer Structures in Electroactive Self-Assembled Monolayers Probed with Photoelectron Spectroscopy”, IMS symposium "Water at interfaces 2018", Okazaki, Japan, Jan. (2019).

[Others (Book, Press release, etc.)]

1. “ナノの光で起こる化学反応 －単一分子の分子結合切断の観測とその機構の解明に成功－”, 理化学研究所報道発表, May 2018.