

**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 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 the molecular adsorption system, in particular the Kondo effect. The characteristic electronic state resulting from the Kondo effect, the so-called Kondo singlet state appears as a sharp peak structure (Kondo peak) at the Fermi level ( $E_F$ ) 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) Molecular adsorption on solid surface: From single molecule to molecular network, and their optical properties [Minhui Lee, Emiko Kazuma, Chi Zhang, Michael Trenary, Jun Takeya, Jaehoon Jung and Yousoo Kim, *J. Phys. Chem. Lett.* 12 (2021) 9868-9873]

The mechanism study of the dissociation of a single-molecule induced by tunneled electrons/holes

chemisorbed on a metal surface, two  $O_2$  species as  $O_2[001]$  and  $O_2[1\bar{1}0]$  molecule depending on the adsorption orientation, is investigated using a scanning tunneling microscope (STM) with DFT calculation. The  $O_2$  dissociation reaction is caused by direct ladder-climbing excitation of the high-order overtones of the O–O stretching mode which is discovered by STM experiment. Moreover, the experiment revealed a more efficient excitation source as tunneled hole using action spectroscopy with STM (STM-AS). The reaction yield for both  $O_2[001]$  and  $O_2[1\bar{1}0]$  molecule is higher at the negative region (Figure 1a and b) than the positive region (Figure 1c and d).

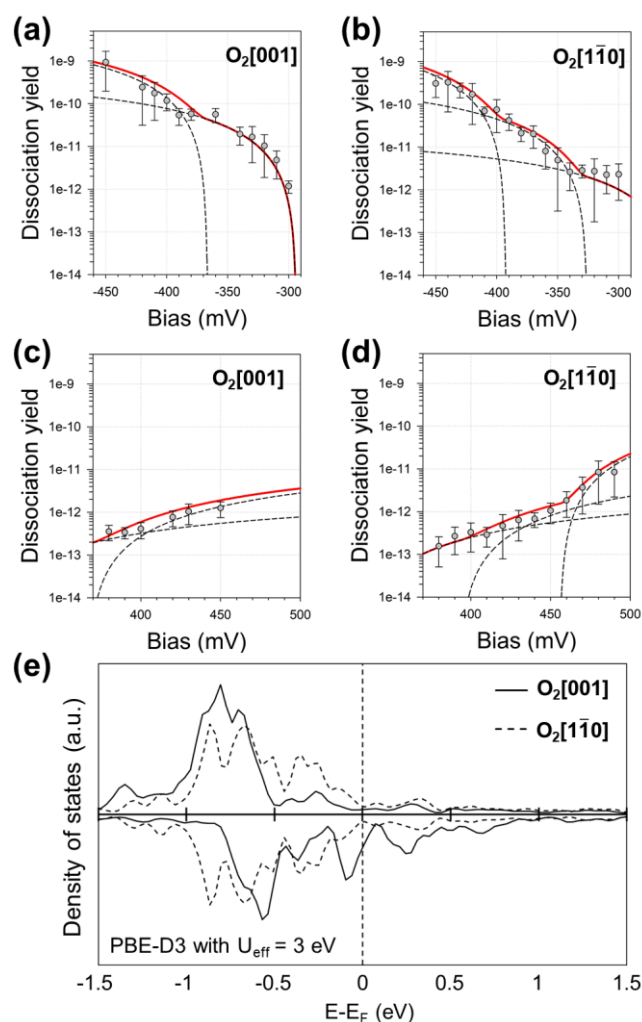


Figure 1. Action spectra for the dissociation of  $O_2[001]$  in the negative (a) and positive (c) bias regions and for the dissociation of  $O_2[1\bar{1}0]$  in the negative (b) and positive (d) bias regions. The initial tunneling current was set to 10 nA. Spectral fitting results are shown as red solid curves. (e) LDOS of an

$O_2[001]$  (solid lines) and  $O_2[1\bar{1}0]$  molecule (dotted lines) on the Ag(110) surface calculated by using PBE-D3. The on-site Coulomb potential was applied to the oxygen 2p states with the DFT+U scheme ( $U_{\text{eff}} = 3 \text{ eV}$ ) Copyright 2021 American Chemical Society

To reveal a deeper understanding, we conduct the density functional theory (DFT) calculations. In the theory of STM-AS based on an adsorbate-induced resonance model (Phys. Rev. B: Condens. Matter Mater. Phys. 2014, 89 (3), 035427), the probability of vibrational excitation depends on the LDOS distribution of the adsorbate at the corresponding energy. Thus, we can interpret the bias polarity dependence of yield based on the distribution of LDOS. The distributions of the LDOS for  $O_2[001]$  and  $O_2[1\bar{1}0]$  obtained from our DFT calculations indicate that the LDOS of an  $O_2$  molecule above the fermi level ( $E_F$ ) is much smaller than that below  $E_F$  (Figure 1e). The lower yield obtained in the positive bias region reflects the low LDOS of the  $O_2$  molecule above  $E_F$ . The DFT calculation explained why hole injection is a more efficient excitation source.

## (2) 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 field as much as 100, TERS measurements still require 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 experimentally obtaining Raman spectra of 4-nitrothiophenol (4-NTP) and

4,4'-dimercaptoazobenzene (DMAB) adsorbed on gold and silver clusters (Figure 2). We found that the simple cluster model is enough to reproduce the experimental Raman spectra (Figure 2b).

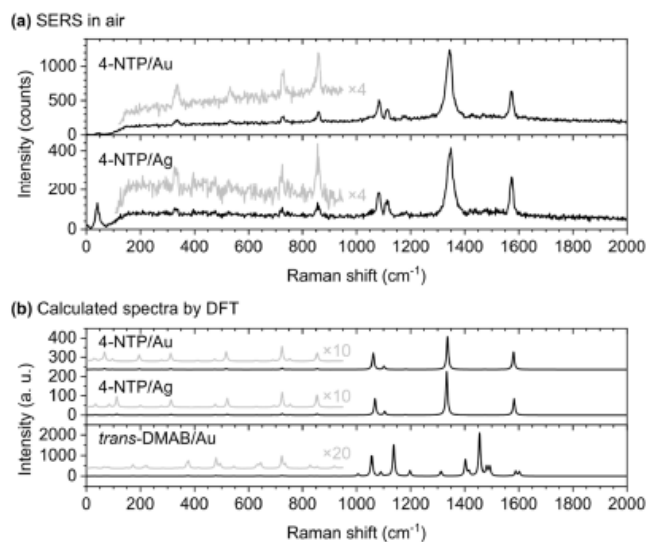


Figure 2. (a) Raman spectra of 4-NTP adsorbed on roughened Au (top) and roughened Ag (bottom) surfaces. The acquisition conditions were excitation at 633 nm with power and exposure time of 8  $\mu\text{W}$  and 3 s (top), and 1  $\mu\text{W}$  and 30 s (bottom), respectively. (b) Calculated Raman spectra of 4-NTP bound to two atoms of Au (4-NTP/Au) or Ag (4-NTP/Ag) and the trans form of DMAB with a sulfur atom on one side bound to two Au atoms (trans-DMAB/Au). The intensities below 950  $\text{cm}^{-1}$  have been magnified by multiplying the numbers noted in each plot to show the weak Raman peaks (light gray).

## (3) On-surface coupling of terminal alkynes and chemical identification of the reaction products [Chi Zhang, Rafael B. Jaculbia, Yusuke Tanaka, Emiko Kazuma, Hiroshi Imada, Norihiko Hayazawa, Atsuya Muranaka, Masanobu Uchiyama, and Yousoo Kim, J. Am. Chem. Soc. 2021, 143, 9461–9467]

We visualized and identified  $\pi$ -skeletons generated by the coupling of terminal alkynes at the single-chemical-bond level both topographically and spectroscopically, and further demonstrated bond control by a combination of scanning tunneling

microscopy/spectroscopy (STM/STS) and tip-enhanced Raman spectroscopy (TERS) techniques. We chose 4,4'-diethynyl-1,1'-biphenyl (DEBP) as the precursor (i.e., terminal alkyne). We precisely revealed the generated sp-sp<sup>2</sup>-carbon skeletons (enyne and cumulene) in real space as evidenced by their characteristic topographies and localized electronic and vibrational properties. Our results clarify the occurrence of an addition reaction (i.e., non-dehydrogenative coupling) in generation of both connections on Ag(111). Furthermore, we show that applying voltage pulses from the STM tip to the target molecules provides bond control, resulting in the dehydrogenation in enyne connections. Density functional theory (DFT) calculations further validate that the lowest unoccupied molecular orbital (LUMO)-derived densities and CC stretching modes of sp-carbon assist recognition of  $\pi$ -skeletons.

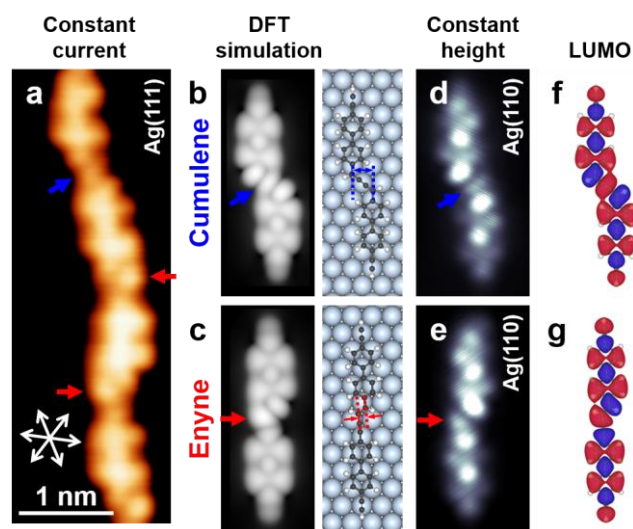


Figure 3. (a) Constant current STM images showing two kinds of connections within a chain obtained with a DEBP-functionalized tip. (b) and (c) Simulated STM images of cumulene and enyne dimers (left panels) based on the corresponding structural models on Ag(111) (right). (d) and (e) Constant height STM images of individual cumulene and enyne dimers on Ag(110) obtained with a DEBP-functionalized tip, respectively. (f) and (g) Calculated LUMO of planar cumulene and enyne dimers in the gas phase.

To distinguish between these two connections formed by coupling of terminal alkynes (i.e., EN and CU indicated by red and blue arrows in Figure 2a, respectively), we performed DFT calculations. For simplicity, dimer structures were optimized on Ag(111), as shown in the right panels of Figure 3b and 3c. The results confirm that EN and CU connections can be attributed to enyne and cumulene, respectively. The calculated offsets in EN and CU connections (indicated in the structural models) are 1.12 and 3.15 Å, respectively, in good agreement with the experimental results ( $1.2 \pm 0.1$  and  $3.3 \pm 0.2$  Å, respectively). Moreover, the enyne dimer adsorbed on Ag(111) is calculated to be more stable than the cumulene dimer by 0.11 eV, in line with the experimental observations that enyne serves as a dominant species. The simulated STM images based on the two structural models are shown in the left panels of Figure 3b and 3c, respectively. In the cumulene connection (with three consecutive double bonds), three central lobes are aligned with similar intervals. In contrast, in the enyne connection (with a double-single-triple conjugation) there is a triangular arrangement of the three lobes. Such electronic features resemble the calculated LUMO densities of the free dimers (Figure 3f and 3g). To examine these features more clearly, we performed STM measurements on the isolated dimers on Ag(110), where the dispersed distribution of DEBP, EN and CU dimers allows direct exploration of single species. Constant height scans of two dimers (Figure 3d and 3e) nicely resolved the characteristic orbital lobes and nodes. Interestingly, LUMO-derived electronic features unambiguously show the orientation of the C(sp<sup>2</sup>)-H ( $\sigma_{CH}$ ) lobes at the centers, which results from the bonding combination of two LUMO orbitals of DEBP molecules. Furthermore, we synthesized 1,3-enyne ex situ and deposited it onto Ag(111), and found it has similar morphology to the in-situ one. The presence of the  $\sigma_{CH}$  features together with the ex-situ comparison supports the occurrence of addition reaction in the formation of both

connections, and our tentative assignment of the new carbon skeletons to enyne and cumulene. By STM-TERS measurements, we then utilized the CC stretching modes of sp-carbon as Raman-active tags in the silent region to locate the enyne  $C\equiv C$  and cumulene  $C=C$  sp-carbon bonds, which further corroborated the scenario discussed above.

#### (4) Photoelectric conversion in single molecule on surface

Light-induced carrier generation have attracted much attention due to its scientific importance and its potential applications such as solar cell, photocatalyst, and photosynthesis. Recent advances of experimental techniques made it possible to observe photocurrent generation in single molecule junctions. In this work, we simulated photocurrent generations for a free-based phthalocyanine (FBPc) molecule adsorbed on a NaCl quadruple-layer films grown on a silver surface.

To analyze the photocurrent generation processes, we had formulated the current flux using Hubbard nonequilibrium Green function (NEGF) method. To carry out the quantitative analysis, first-principles calculation based on the density functional theory (DFT) and time-dependent DFT (TDDFT) had been performed to obtain molecular electronic structure and vibrational frequencies. Other parameters used in the simulations, e.g. image interactions, were estimated based on the previous studies. In this financial year, we conducted detailed investigation of the dependence of photocurrent direction on the position of the STM tip. We revealed that there is more than one process of photocurrent generations. Since molecular orbitals contributed to different processes have different spatial distributions, the direction and amount of photocurrent change depending on the tip position owing to the variation of the molecule-tip coupling strengths. Our study would make significant contributions to obtain a fundamental understanding of the photocurrent generations at the molecule/substrate interfaces,

whereby this would provide useful knowledge for improving the device performance.

#### 4. Conclusion

We have tried to examine a variety of molecular behaviors on the surface in FY2021. Our theoretical studies combined with experiments in FY2021 provide deep insight into a variety of chemical and physical phenomena on solid surface: (1) efficient excitation carriers for surface reaction dynamics, (2) Raman spectra of self-assembled monolayers on gold electrode, (3) Chemical identification of the reaction products, (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 the 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 the following factors: (i) charge transfer between adsorbates and oxide-metal interface, which is closely correlated with the electronic affinity (EA) of adsorbate and work function reduction, (ii) adhesion between oxide and metal layers with strong polaronic distortion, (iii) film thickness, and (iv) the chemical composition of the oxide surface. Therefore, we will continue our work to find a way for controlling the chemical reactivity using theoretical and experimental studies. In FY2022, we will extend our study into various chemical reactions, such as dissociation and hopping, on ultrathin MgO film using combined STM and DFT methodology. We

expect the influence of charge transfer between the oxide surface and the oxide-metal interface. The other branch of our study is exploring the single-atom catalyst on the ultrathin oxide film, which is now widely studied due to its prominent importance in a heterogeneous catalyst. Therefore, we will introduce a 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. In FY2022, the study on titania will be intensively performed to find a proper supporting substrate to efficiently realize ultrathin titania film. 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 a 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  $\pi$ -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. In FY2022, we study the reverse stability of DAE on the metal surface compared to the gas phase by investigating of the electronic structure of DAE using DFT

calculation and STM experiment.

(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 result 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 FY2022, we are going to theoretically investigate (1) our very recent experimental finding of well-ordered graphene functionalization with OH group, 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) Bandgap opening at periodic metal cluster on graphene: the first-principle study of localized electron distribution and the band structure

Graphene has been spotlighted in various research areas as a representative two-dimensional material. Since it has unique properties, many researchers study to utilize it in a wide field. Although graphene

has superior conductivity, it was difficult to apply in a semiconductor device because pristine graphene has no bandgap. Therefore, there are various attempts to open bandgap through chemical modification (e.g., graphene nanoribbon, graphene nanomesh, etc.).

Our group proposed van Hove singularity in graphene nanowrinkle (GNW) by scanning tunneling microscopic study (Nat. Commun. 2015, Hyunseob Lim, et al.). This observation is strong evidence of quantum confinement in GNW. However, the physical origin of confinement by the interface with metallic surrounding regions has been still unveiled. For this reason, we will conduct density functional theory (DFT) calculations to observe the band structure of GNW and electron behavior at the localized region. We expect that our structure not only can open bandgap but also provides a fundamental understanding of the interaction between graphene and periodic metal clusters.

#### (5) 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. In addition, we will also simulate the resonance Raman spectra of relatively large molecules using Gaussian package.

#### (6) On-surface photo-induced reactions and syntheses

As mentioned in the above section, a thermal-induced on-surface synthesis strategy was applied to trigger the addition reaction constructing hybrid sp-sp<sup>2</sup>-carbon skeletons (i.e., enynes and cumulenes). The combination of STM/STS and TERS affords characterization of submolecular topographies and, more importantly, detection of characteristic electronic and vibrational features

involved, which leads to precise chemical identification. It thus assists the discrimination of reaction schemes involved, and a non-dehydrogenative direct addition reaction scenario is revealed in the coupling of terminal alkynes on Ag(111). In FY2022, we plan to further deeply explore some other topics related to the on-surface synthesis from the following prospects: (1) adsorption configurations; (2) molecule-molecule interactions and molecule-substrate interactions; (3) electronic and magnetic properties; (4) possible reaction pathways.

#### (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 and photocurrent generation in single molecule under the light irradiation can be investigated with the aid of STM and optical measurements, enabling us to investigate the energy conversion processes with submolecular spatial resolution in a well-defined manner. Especially, we focus on electron correlations in these 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 under applied bias and/or light irradiation. 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 energy conversion and in the designing of novel functional materials for organic (opto)electronic devices.

6. If no job was executed, specify the reason.

**Fiscal Year 2021 List of Publications Resulting from the Use of the supercomputer**

**[Paper accepted by a journal]**

1. Chi Zhang, Rafael B. Jaculbia, Yusuke Tanaka, Emiko Kazuma, Hiroshi Imada, Norihiko Hayazawa, Atsuya Muranaka, Masanobu Uchiyama, and Yousoo Kim, "Chemical identification and bond control of  $\pi$ -skeletons in a coupling reaction" *J. Am. Chem. Soc.*, **143**, 9461 (June, 2021)
2. Misun Hong, Yasuyuki Yokota, Raymond A. Wong, Norihiko Hayazawa, Emiko Kazuma, Yousoo Kim "Underpotential Deposition of Silver on Gold for Surface Catalysis of Plasmon-Enhanced Reduction of 4-Nitrothiophenol", *J. Phys. Chem. C*, **125** (30), 16569–16575 (July, 2021).
3. Yasuyuki Yokota, Raymond A. Wong, Misun Hong, Norihiko Hayazawa, Yousoo Kim "Monatomic Iodine Dielectric Layer for Multimodal Optical Spectroscopy of Dye Molecules on Metal Surfaces", *J. Am. Chem. Soc.*, **143** (37), 15205–15214 (September, 2021).
4. Minhui Lee, Emiko Kazuma, Chi Zhang, Michael Trenary, Jun Takeya, Jaehoon Jung and Yousoo Kim, *J. Phys. Chem. Lett.* **12**, 9868-9873 (October, 2021).

**[Oral presentation]**

1. 横田泰之, "電気化学界面の微視的理解に向けた in-situ 及び ex-situ 手法の開拓: 近接場分光と光電子分光の応用", 第 76 回物理学会年次大会, 先進的計測・理論による表面界面ナノ研究の新展開, オンライン, 2021 年 3 月.
2. 横田泰之他, "大気中探針増強ラマン分光における自己収束的探針先端加工: 増強効果と STM 像への影響", 電気化学会第 88 回大会, オンライン, 2021 年 3 月.
3. Misun Hong 他, "Ag Underpotential Deposition at Thiolate/Au Interface on Surface-Enhanced Raman Spectroscopy", 電気化学会第 88 回大会, オンライン, 2021 年 3 月.
4. Yasuyuki Yokota 他, "Development of Tip-Enhanced Raman Spectroscopy as an Analytical Tool for Electrochemical Interfaces", International Symposium on Surface Science (ISSS-9), Online, Japan, December 2021.
5. Single-molecule studies of plasmon-induced dissociation reactions on metal surfaces using STM, Emiko Kazuma, Minhui Lee, Jung, Jaehoon, Michael Trenary and Yousoo Kim, Pacificchem 2021, Online, December 2021
6. STM study of dissociation mechanism for O<sub>2</sub> chemisorbed on Ag(110), Minhui Lee, Emiko Kazuma, Chi Zhang, Michael Trenary, Jun Takeya, Jaehoon Jung and Yousoo Kim, 表面・界面スペクトロスコピー2021, オンライン, December 2021

**[Poster presentation]**

1. Bandgap opening at periodic metal cluster on graphene: First principle study of localized electron distribution and band structure, Jong-Guk Ahn, Jaehoon Jung, Hyunseob Lim, RPGR2021 (The 12th Recent progress in graphene and two-dimensional materials research conference), Seoul, Korea, Oct. (2021)
2. High-order overtone-mediated dissociation mechanism of a single O<sub>2</sub> molecule chemisorbed on Ag(110), Minhui Lee, Emiko Kazuma, Chi Zhang, Michael Trenary, Jun Takeya, Jaehoon Jung, and Yousoo Kim, The 9th International Symposium on Surface Science, Online, Dec. (2021)