

Project Title:

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

Name:

○ Yousoo Kim (1,2), Jaehyun Bae (1), Kuniyuki Miwa (1,3), Yasuyuki Yokota (1), Chi Zhang (1,4), Hyunseob Lim (1,5), Jong-Guk Ahn (1,5), Jaehoon Jung (1,6), Keita Tanaka (1), Minhui Lee (2)

Laboratory at RIKEN:

(1) Cluster for Pioneering Research, Surface and Interface Science Laboratory

(2) Department of Applied Chemistry, The University of Tokyo

(3) Department of Theoretical and Computational Molecular Science, Institute for Molecular Science

(4) Interdisciplinary Materials Research Center, Tongji University

(5) Department of Chemistry, Gwangju Institute of Science and Technology

(6) Department of Chemistry, University of Ulsan

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 3) modification of physical properties of 2D film. 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) (1) Molecular adsorption on solid surface: From single molecule to molecular network, and their optical properties [Chem. Rec. e202200011, 1-12 (March, 2022)]

The mechanism study of dissociation induced by electron and plasmon of a single-molecule strongly chemisorbed on a metal surface was investigated using a scanning tunneling microscope (STM) with DFT calculation. We review single-molecule studies of O_2 dissociation on Ag(110) induced by various excitation sources using a STM. The comprehensive studies based on the STM and DFT calculations provide fundamental insights into the excitation pathway for the dissociation reaction.

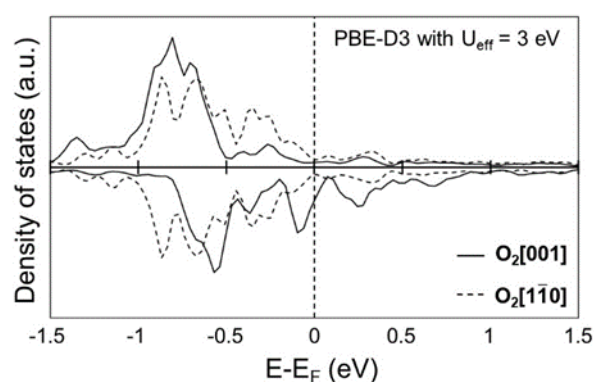


Figure 1. The calculated LDOS of an $O_2[001]$ (solid lines) and $O_2 [1 \bar{1} 0]$ molecule (dotted lines) chemisorbed on the Ag(110) surface.

The STM-action spectroscopy experiments combined with DFT calculations revealed that the local density of states (LDOS) distribution near E_F shows why the reaction efficiency strongly depended on the choice of electrons or holes for both plasmon and tunneled electrons/holes-induced dissociation. The significant finding by the combination of STM and DFT calculations at a single-molecule level is that both the principal mechanism of molecular excitation by various excitation sources and the yield of the dissociation reaction depends on the degree of hybridization between the molecular orbitals and metal states.

(2) Photocurrent generation in single molecule on surface [Nature 603, 829-834 (March, 2022)]
Generation of electric current induced by light irradiation have attracted much attention owing to its scientific importance and its potential

applications such as solar cell, photocatalyst, and photosynthesis. With the recent advances of experimental techniques in the fields of surface science and laser technology, it becomes 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 thin 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. We had also investigated the dependence of photocurrent direction on the position of the STM tip. In this financial year, we conducted the further detailed analysis on the obtained results. Especially, the dependence of the photocurrent direction on the STM tip position were revealed, and its origin was explained well. 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.

(3) On-surface coupling of terminal alkynes and chemical identification of the reaction products [J. Am. Chem. Soc. 144 10282-10290 (May, 2022)]

In FY2022, we systematically studied on-surface reactions of terminal alkynes and regulation of the reaction pathways under different experimental conditions. We have successfully steered on-surface reaction pathways of terminal alkynes by introducing O₂ into the molecular system and explored the catalytic performances and reaction

mechanisms of oxygen species involved in the C–H activation processes.

Selective regulation of target chemical reactions is crucial in chemistry. Oxygen, as a dominant reagent in the ubiquitous oxidative chemistry, has been reported to induce structural transformation, oxidize organic adlayers, and have catalytic effects in facilitating self-metalation and metal replacement processes on surfaces as well as on-surface synthesis. However, the unique catalytic performances and reaction mechanisms of oxygen species remain elusive, which, yet, are of utmost importance in providing fundamental understanding in the reaction selection and regulation. In this study, by combining STM imaging/manipulations and DFT calculations, we have clarified that both molecular O₂ and atomic O can efficiently steer the reaction pathways of terminal alkynes on Ag(111) from C–C coupling to dehydrogenative reaction (i.e., C–H activation) with high selectivity.

We chose 4,4'-diethynyl-1,1'-biphenyl (DEBP) as the molecular precursor with terminal alkynyl groups at both sides. By controllably introducing oxygen species into the molecular system, we have shown that an O₂-induced C–H activation process is applicable for both DEBP and DEBP-based more complicated oligomers (with terminal alkynyl groups) on Ag(111) as well as DEBP on Au(111). Interestingly, by precisely controlling the active oxygen species, we have verified that both molecular and atomic oxygen can effectively lead to the H atom abstraction (via an associative or dissociative mechanism, respectively) followed by adatom addition forming OM structures.

With the aim of understanding the drastic change in reaction performances and revealing the reaction mechanisms including the role of oxygen species in the processes, further *in-situ* STM experiments and DFT calculations were carried out. By applying a

voltage pulse, we successfully triggered the dehydrogenation locally (Fig. 2a-b). An abrupt drop was observed in the current trace (as indicated by the arrow in Fig. 2c), and a dark depression appeared at the terminus of the DEBP molecule (as pointed out by the white arrow in Fig. 2b) indicating the dehydrogenation.

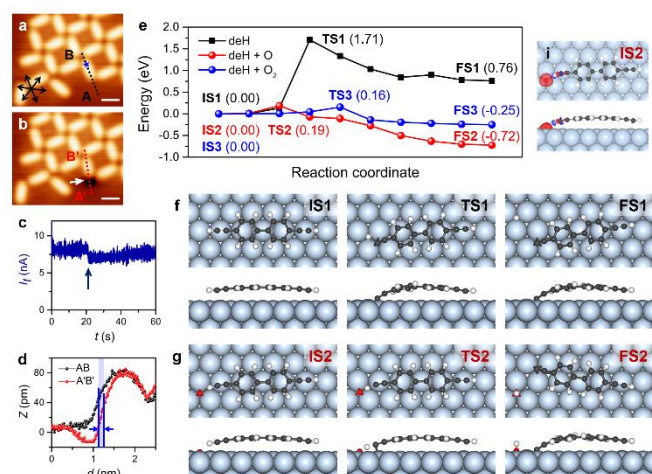


Figure 2. *In-situ* dehydrogenation in experiment and corresponding DFT calculated C-H activation process without or with oxygen species, respectively. (a, b) Sequential STM images gained before and after applying a voltage pulse to a single DEBP molecule at the position marked by the star. (c) Current trace of the *in-situ* dehydrogenation process induced by the voltage pulse, where an abrupt change was pointed out by the arrow. (d) Line-scan profiles along the dotted lines AB (in black) and A'B' (in red) as depicted in (a) and (b), respectively. The difference in lengths is highlighted in blue. (e) Energy diagram of the DFT calculated dehydrogenative reaction pathways on Ag(111) without oxygen species and with O or O₂ species, respectively. The corresponding initial states (IS), transition states (TS) and final states (FS) are marked along the pathways, and their energies are provided with respect to that of the respective IS involved. (f, g) Top and side views of the corresponding structural models involved in the pathways (f) without any oxygen species; and (g) with O atom. C: grey; H: white; O: red; Ag: light blue. (i) Charge-density-difference map showing the charge transfer between a DEBP molecule and an O

atom, where red and blue indicate charge accumulation and depletion, respectively.

Thereafter, we conducted extensive DFT calculations to search the reaction pathways for identifying the role of oxygen species in the C-H activation processes. In the absence of oxygen, the C-H cleavage process is calculated to be endothermic with a reaction barrier of ~ 1.71 eV (Fig. 2e). Interestingly, the participation of oxygen species (both atom and molecule) can drastically reduce the reaction barrier of C-H activation to ~ 0.19 eV and ~ 0.16 eV (Fig. 2e), respectively, by interacting with the terminal groups via C-H \cdots O hydrogen bonds (Fig. 2i), and the oxygen-induced C-H activation becomes exothermic. It thus provides the possibility to steer the reaction pathway from the addition reaction to C-H activation. Herein, oxygen species act as reactants which are able to facilitate the C-H activation of terminal alkynyl groups by abstracting H atoms in both associative and dissociative mechanisms.

(4) Investigation of 2D material growth behavior [ACS Nano 17, 2, 1196-1205 (January, 2023)]

To investigate synthesis behavior of MoS₂ on C-plane sapphire (α -Al₂O₃), DFT calculations also have been conducted. A highly reproducible route for the epitaxial growth of single-crystalline monolayer MoS₂ on a C-plane sapphire substrate was developed using vapor-pressure-controllable inorganic molecular precursors MoOCl₄ and H₂S. Microscopic, crystallographic, and spectroscopic analyses indicated that the epitaxial MoS₂ film possessed outstanding electrical and optical properties, excellent homogeneity, and orientation selectivity. The systematic investigation of the effect of growth temperature on the crystallographic orientations of MoS₂ revealed that the surface termination of the sapphire substrate with respect to the growth temperature determines the crystallographic orientation selectivity of MoS₂ (Figure X). Our

results suggest that controlling the surface to form a half-Al-terminated surface is a prerequisite for the epitaxial growth of MoS₂ on a C-plane sapphire substrate. The insights on the growth mechanism, especially the significance of substrate surface termination, obtained through this study will aid in designing efficient epitaxial growth routes for developing single-crystalline monolayer transition metal dichalcogenides.

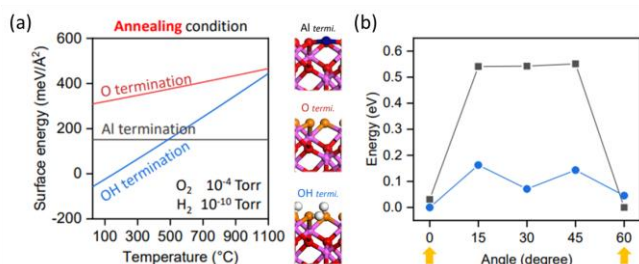


Figure X. (a) Surface energies of the various terminated C-plane sapphire surfaces, half-Al-termination, (Al-3O-Al) (black); O-termination, (3O-Al-Al) (red); OH-terminations, 3H-(3O-Al-Al) (blue) under annealing conditions ($O_2 = 10^{-3}$ Torr, $H_2 = 10^{-10}$ Torr). (b) Binding energy as a function of the relative angle between the MoS₂ seed and the half-Al-terminated surface (black) and OH-terminated surface (blue).

4. Conclusion

We have tried to examine a variety of molecular behaviors on the surface in FY2022. Our theoretical studies combined with experiments in FY2022 provide deep insight into a variety of chemical and physical phenomena on solid surface: (1) efficient excitation carriers for surface reaction dynamics, (2) photocurrent generation in single molecule on surface, (3) the catalytic performances and reaction mechanisms of oxygen species involved in the C-H activation processes, (4) Chemical potential dependent changing of surface termination. We expect that our results can provide new perspective to develop a potential strategy for controlling chemical/physical properties of surface system including adsorbed single-molecule

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 FY2023, 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) On-surface molecular reactions and syntheses

As mentioned above, we have successfully steered on-surface reaction pathways of terminal alkynes by introducing O₂ into the molecular system and explored the catalytic performances and reaction mechanisms of oxygen species involved in the C–H activation processes. As a step further, we plan to 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 and mechanisms.

(3) Investigation of electronic structure of 2D materials

Theoretical principles for explaining the features of edge-free wrinkled graphene have not yet been established. Therefore, based on the experimental observations, we will perform DFT calculations to verify the properties of graphene nano-wrinkle (GNW) in metals with a model system. We continue to strive to reveal that it can play a crucial role in inducing interfacial interactions and quantum confinement between graphene and substrates.

(4) Investigation of electronic structures and properties of thermally activated delayed fluorescence emitter.

Organic electronic materials have been estimated as an important component to be used in various organic semiconductor industries such as organic light-emitting diode (OLED), organic LASER diode (OLD) or organic solar cell (OSC). To increase the out-coupling efficiency of electroluminescence devices utilizing organic emitter, harvesting of triplet excitons generated by spin statistics has been a very important issue because most of the excitons in the triplet state are annihilated by non-radiative decay. A common strategy for harvesting triplets in

pure organic materials minimizes the gap between singlet and triplet states by separating the HOMO and LUMO of a molecule, leading to a reverse intersystem crossing. In this way, thermally activated delayed fluorescence (TADF) materials can theoretically obtain up to 100% internal quantum efficiency. Although the distribution of the frontier molecular orbital of a molecule is very important to determine the TADF property, the analysis of the electrical structure has mostly relied on density functional theory (DFT) calculations so far. In FY2023, (1) we will analyze the orbital distributions and electrical properties of TADF molecules with DFT calculation, and (2) we will compare the result with scanned images using scanning tunneling microscope (STM) of the TADF molecules. This comparison will be good standard to evaluate the reliability of DFT calculations for the orbital distribution in TADF molecules and to propose new molecular designs with optimized TADF properties.

(5) On-surface synthesis of single-molecule magnets (SMMs)

SMMs are attractive molecular materials, which could potentially lead to the development of ultra-high density memory devices. The clean metal surface in the UHV environment is ideal for the generation of new types of SMMs, which decompose or cannot exist in ambient conditions. In FY2023, we are going to do ab-initio calculation at casscf/caspt2, casscf/nevpt2 level to predict the magnetic properties of SMM candidates. We will also perform vibrational frequency analysis of surface bound molecules by DFT calculation to analyze the on-surface reaction by comparing with the experimental SERS (surface enhanced raman spectroscopy), TERS (tip enhanced raman spectroscopy) data.

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

Fiscal Year 2022 List of Publications Resulting from the Use of the supercomputer

If there are no research achievement, please delete this page and later.

Note

- Applicable publications
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 - ◇ Author, title, journal name, volume, issue and page number, and publication date
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 - ◇ Author, title, name of the meeting, presentation date, and place
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- If there are no applicable research achievements, you can delete the items.

[Paper accepted by a journal]

1. Minhui Lee, Emiko Kazuma, Jaehoon Jung, Michael Trenary, Yousoo Kim "Dissociation of Single O₂ Molecules on Ag(110) by Electrons, Holes, and Localized Surface Plasmons", *Chem. Rec.* e202200011 ,1-12, (March, 2022)
2. Miyabi Imai-Imada, Hiroshi Imada, Kuniyuki Miwa, Yusuke Tanaka, Kensuke Kimura, Inhae Zoh, Rafael B. Jaculbia, Hiroko Yoshino, Atsuya Muranaka, Masanobu Uchiyama, Yousoo Kim, "Orbital-resolved visualization of single-molecule photocurrent channels", *Nature* 603, 829-834, (March, 2022)
3. Chi Zhang, Emiko Kazuma, Yousoo Kim, "Steering the reaction pathways of terminal alkynes by introducing oxygen species: From C–C coupling to C–H activation", *J. Am. Chem. Soc.* 144 10282-10290, (May, 2022)
4. Younghee Park, Chaehyeon Ahn, Jong-Guk Ahn, Jee Hyeon Kim, Jaehoon Jung, Juseung Oh, Sunmin Ryu, Soyoung Kim, Seung Cheol Kim, Taewoong Kim, Hyunseob Lim, "Critical Role of Surface Termination of Sapphire Substrates in Crystallographic Epitaxial Growth of MoS₂ Using Inorganic Molecular Precursors", *ACS Nano* 17, 2, 1196-1205 (January, 2023)

[Conference Proceedings]

[Oral presentation]

1. Miyabi I-Imada, Hiroshi Imada, Kuniyuki Miwa, Yusuke Tanaka, Kensuke Kimura, Inhae Zoh, Rafael Jaculbia, Hiroko Yoshino, Atsuya Muranaka, Masanobu Uchiyama, Yousoo Kim, "Orbital-resolved visualization of single-molecule photocurrent channels", The 22nd International Vacuum Congress (IVC-22), September 11-16, 2022, Sapporo Convention Center, Sapporo, Japan.

Usage Report for Fiscal Year 2022

2. Kuniyuki Miwa, “Theoretical investigation of optoelectronic conversion in single molecules on solid surfaces”, IMS-ICAT Joint Symposium Surface Science for Catalysis, October 11, 2022, Creative Research Institution, Hokkaido University, Sapporo, Japan.

[Poster presentation]

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