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 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, FHI-aims, 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.

3. Result

(1) Anomalous one-dimensional quantum confinement effect in graphene nanowrinkle [Phys. Rev. B. 108 (2023) 045412]

Graphene is one of the most popular two-dimensional materials. It has unique properties, such as conductivity, mechanical strength, and thermal stability. Although graphene has superior conductivity, it was difficult to apply semiconductor devices because pristine graphene has no bandgap. Therefore, there are various attempts to open bandgap through chemical modification (e.g., graphene nanoribbon, graphene nanomesh). We report the van Hove singularity in graphene nanowrinkle (GNW) structure at Ni(111) surface by scanning tunnelling microscopy, which is strong evidence of quantum confinement effect.

To investigate those van Hove singularities, we conducted systematic DFT calculations with GNW/Ni(111) and GNW/Cu(111). Charge difference map and orbital projected band structure revealed different interactions between graphene and each metal. We unveil that the interfacial interaction between the graphene and the substrate plays a crucial role in leading to quantum confinement. The longitudinal direction and the effective confined length were investigated as key parameters to control the electronic structure of graphene by corrugation engineering. (Figure 1a) Furthermore, a series of standing waves corresponding to the "particle in a box" model was also confirmed by the charge densities of GNW. (Figure 1b,c) Our computational studies rationalize the pseudo-1D quantum confinement in GNW, indicated by the vHS, and provide deep insight into the electronic behaviors of the graphene-derived electronic materials through electronic structure engineering.

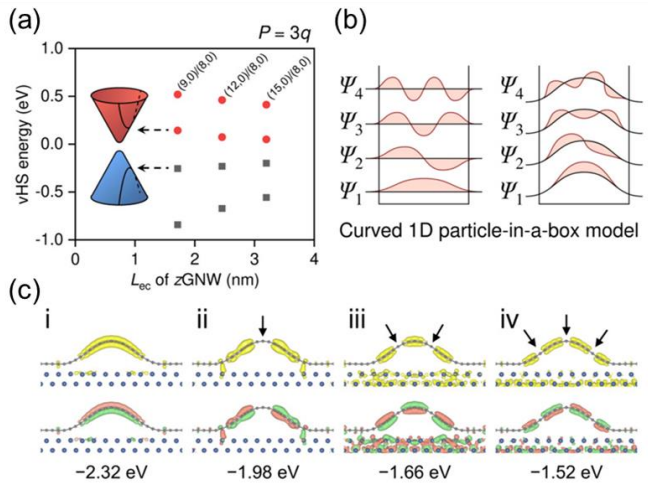

Figure 1 (a) Energy level of vHS as a function of the effective confinement length (L_{ec}) for zGNW. (b)Schematic illustration of wavefunctions in 1D particle in a box model for flat and curved structures. (c) (Top) Band-decomposed charge densities from the specific energy level at the point for one of model of zGNW/Ni and (bottom) each wavefunction.

(2) Real-space observations of multiple reaction pathways enabled by plasmonic hot carriers [J. Phys. Chem. C 127 (2023) 10953]

The detailed mechanism of various surface reactions of a single O_2 molecule induced by electron and plasmon was investigated when a single molecule was strongly chemisorbed on a metal surface. Based on the comprehensive investigation by a scanning tunneling microscope (STM) with DFT calculation, we handled multiple reaction pathways, rotation and dissociation, of a single O_2 molecule 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. 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 multiple reaction pathways. In addition, the yield of the dissociation reaction depends on the degree of hybridization between the molecular orbitals and metal states was suggested the efficient excitation source.

(3) Mechanism study of CO hopping on ultra-thin MgO film on Ag(100) [*In preparation*]

The unusual excitation pathway important for fundamental study and industrial investigation to increase the reactivity and reduce the side reaction. The understanding of various reaction pathways helps us to think widely on chemical reaction. Regulating the interfacial interaction between molecule and surface shows variety of reaction pathways. Introducing the ultra-thin insulating film between molecule and metal surface will reduce strong orbital hybridization and ultra-thin insulating film increases catalytic properties of insulating material compared with bulk. In this study, we investigated the single CO molecule on 2 monolayer (ML) of MgO/Ag(100) by combination of STM and DFT calculations. (Figure 2)

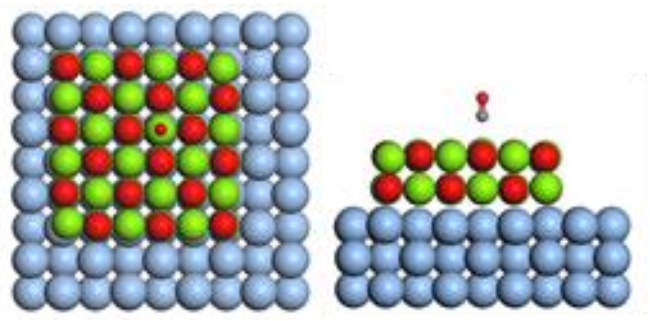

Figure 2. Optimized structure of CO molecule on island of 2ML MgO/Ag(100).

There were three different reaction pathways to induced the CO hopping which are revealed from STM-AS. The anharmonic coupling among vibration mode of CO molecule and RC mode induces the surface reaction, hopping. Not only the vibrational excitation of molecule but also the phonon-mode excitation of thin layer MgO induces the CO hopping. The detailed reaction mechanism was supported DFPT calculation to consider the phonon-mode of MgO.

4. Conclusion

We have tried to examine a variety of molecular behaviors on the surface in FY2023. Our theoretical studies combined with experiments in FY2023 provide deep insight into a variety of chemical and physical phenomena on solid surface: (1) interaction between graphene-metal and electronic motion at nanosized graphene structure, (2) efficient excitation source for O_2 dissociation reaction, (3) reaction barrier and pathways considering coupling between surface phonon and vibration mode of single molecule. 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 FY2024, 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 FY2024, 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) Investigation of thin sp^3-hybridized system

Wurtzite boron nitride (w-BN) has exceptional thermal stability, high electrical insulation, and high chemical resistance, and it is suitable for various applications in the fields of electronics, energy, and materials science. w-BN can be used as a substrate for electronic devices such as high-frequency transistors and high-power diodes, due to its high thermal stability and electrical insulation properties. It is important to note that the properties of w-BN vary depending on the synthesis conditions, and so the optimal application conditions should be carefully selected based on the desired properties and requirements. However, it is difficult to achieve atomically thin film due to its nature of sp^3 hybridization. Therefore, we will investigate new synthetic ways to obtain thin w-BN from hexagonal boron nitride (*h*-BN) via periodic functionalization by DFT calculation.

(3) 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 FY2024, (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.

(4) 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 FY2024, 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 2023 List of Publications Resulting from the Use of the supercomputer

[Paper accepted by a journal]

1. Emiko Kazuma, Minhui Lee, Jaehoon Jung, Michael Trenary, Yousoo Kim “Real-space observations of multiple reaction pathways enabled by plasmonic hot carriers”, *J. Phys, Chem. C* 127, 10953 (June, 2023)
2. Jong-Guk Ahn, Jee Hyeon Kim, Minhui Lee, Yousoo Kim, Jaehoon Jung, Hyunseob Lim “Anomalous one-dimensional quantum confinement effect in graphene nanowrinkle”. *Phys. Rev. B* 108, 045412 (July 2023)

[Conference Proceedings]

[Oral presentation]

1. Minhui Lee, “Mechanism study of a chemisorbed O_2 molecule on Ag(110) induced by high-order overtone excitation using STM”, AVS 69, Portland, OR, US, November 5-10 (2023)

[Poster presentation]

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