Usage Report for Fiscal Year 2022

**Project Title:**

# Exploring on-surface photo-synthesis under ultrahigh vacuum conditions

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

On-surface synthesis has been demonstrated as a promising bottom-up strategy to construct robust covalent nanostructures with desired patterns and efficient charge transport. Photochemical-induced covalent-bonding creation reaction (defined as “photo-synthesis” here) is highly limited on surface under ultrahigh vacuum (UHV) conditions in comparison with thermal-driven synthesis and is expected to have an increasingly broad prospect as is in conventional solution chemistry. By combination of scanning tunneling microscopy/spectroscopy (STM/STS) and density functional theory (DFT) calculations, my research has been mainly focusing on exploration of on-surface photo-synthesis under UHV conditions both experimentally and theoretically. The ultimate goal of this project is to gain deep understandings of the chemical and physical properties of adsorbates on the surface and unravel the underlying reaction mechanisms with the help of theoretical calculations.

## 2. Specific usage status of the system and calculation method

I have been investigating the relevant molecular systems on metal surfaces by combination of STM/STS observations and theoretical calculations. Most of the calculations were performed in the DFT framework using the Vienna ab initio simulation package (VASP). The projector-augmented wave method was used to describe the interactions between ions and electrons. The Perdew−Burke−Ernzerhof generalized gradient approximation exchange-correlation functional was employed, and van der Waals interactions were included using the dispersion-corrected DFT-D3 method of Grimme. The atomic structures were relaxed using the conjugate gradient algorithm scheme as implemented in the VASP code until the forces on all unconstrained atoms were ≤ 0.02 eV/Å. Plane waves were used as a basis set with an energy cutoff of 450 eV. Ag(111) substrate was modelled by four-layered slabs separated by a ~20 Å vacuum region for the structural models, where the bottom two layers were fixed. Simulated STM images were obtained based on the Tersoff−Hamann method. The climbing-image nudged elastic band (CI-NEB) was applied to locate the transition states, and the transition paths were optimized until the forces acting on the path were ≤ 0.03 eV/Å.

## 3. Result

In FY2022, I systematically studied on-surface reactions of terminal alkynes and regulation of the reaction pathways under different experimental conditions. I have successfully steered on-surface reaction pathways of terminal alkynes by introducing $O_2$ 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 $O_2$ 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 $O_2$-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. 1a-b). An abrupt drop was observed in the current trace (as indicated by the arrow in Fig. 1c), and a dark depression appeared at the terminus of the DEBP molecule (as pointed out by the white arrow in Fig. 1b) indicating the dehydrogenation.

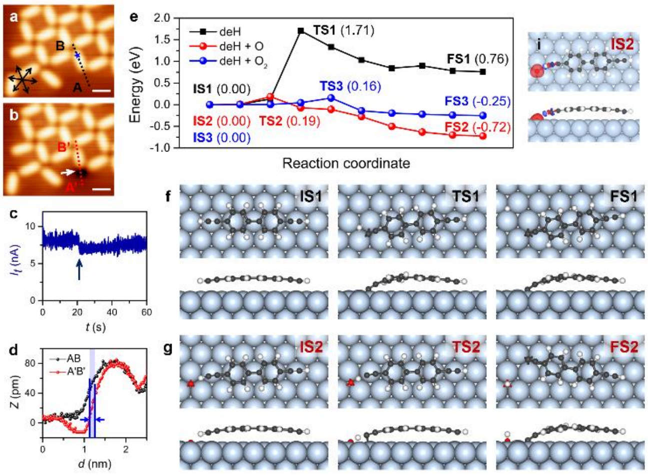

Figure 1. *In-situ* dehydrogenation in experiment and corresponding DFT calculated C–H activation process without or with oxygen species, respectively. (a, b) Sequential STM images gained before and after applying a voltage pulse to a single DEBP molecule at the position marked by the star. (c) Current 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 $O_2$ 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. 1e). 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. 1e), respectively, by interacting with the terminal groups via C−H···O hydrogen bonds (Fig. 1i), 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. Conclusion

In conclusion, I have corroborated both experimentally and theoretically that introduction of oxygen species (both atomic O and molecular $O_2$) can significantly steer the reaction pathway, which displays the versatility of this catalytic strategy in selectively regulating and highly accelerating on-surface reaction pathways. Our study also provides fundamental insights into reaction mechanisms between gas molecules and preabsorbed surfaces and paves way for understanding many key interfacial chemical processes such as partial oxidation and epoxidation.

## ５. Schedule and prospect for the future

In FY2023, I plan to further deeply explore some other topics related to the on-surface photo-induced 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.

Additionally, I would like to continue using the system for the FY2023.

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

### [Paper accepted by a journal]

Chi Zhang, Emiko Kazuma, and 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 (May, 2022)