Usage Report for Fiscal Year 2018

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 a promising bottom-up strategy to construct robust covalent nanostructures with desired patterns and efficient charge transport, especially under ultrahigh vacuum (UHV) conditions. However, photochemical-induced covalent-bonding creation reaction (defined as "photo-synthesis" here) is highly limited on surface under 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 probe microscopy/spectroscopy and theoretical calculations, my research is mainly focusing on exploration of on-surface photo-synthesis under UHV conditions both experimentally and theoretically.

2. Specific usage status of the system and calculation method

In my study, the calculations were performed in the framework of density functional theory (DFT) by using the Vienna ab initio simulation package (VASP). The projector-augmented wave method was used to describe the interaction 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 ≤ 0.03 eV/Å. Plane waves were used as a basis set with an energy cutoff of 400 eV for the models. The simulated STM images were obtained by the Hive program 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 typically ≤ 0.03 eV/Å.

3. Result

In this year, I have been calculating one system concerning on-surface synthesis. The adsorption configurations of the molecular precursors, intermediate states, final covalent-bonded nanostructures and the corresponding self-assembled structures have been calculated on the metal substrates. The primary intermolecular interactions involved in these structures have been revealed. Direct comparisons of the DFT-simulated STM images and the STM observations have been gained to further confirm the rationality of hypothesis. The CI-NEB has been used to find the transition states, and subsequently, the possible reaction pathways with the corresponding reaction barriers have been discovered from the point of theoretical calculations. Based on both experimental and theoretical indications, the underlying mechanisms of the on-surface reaction process have been revealed to provide an atomic-scale understanding of the overall reaction process.

４． Conclusion

In FY2018, I have tried to combine the theoretical calculations with the STM experiments to examine a variety of molecular behaviors and reaction pathways towards target structures on the metal surfaces. Such kinds of study made a good combination of real-space observation and theoretical prediction to provide fundamental understandings into the underlying mechanisms in the on-surface reaction processes on the metal surface.

５． Schedule and prospect for the future

In FY2019, 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 FY2019 to finish the current project. Hopefully, one paper will be published in the FY2019.

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

[Poster presentation]

Chi Zhang, Emiko Kazuma and Yousoo Kim, Surface-mediated stepwise evolution of chiral organometallic networks, 14th International Conference on Atomically Controlled Surfaces, Interfaces and Nanostructures (ACSIN-14), October 22, Sendai Japan 2018.