

Project Title:**Exploring on-surface photo-synthesis under ultrahigh vacuum conditions****Name:**

○Chi ZHANG

Laboratory at RIKEN:**Surface and Interface Science Laboratory**

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. Raman spectra were calculated using the Gaussian 16 program package. The hybrid functional PBE0 with a 6-31G(d,p) basis set was applied for the vibrational frequency calculations. All the vibrational frequencies were scaled by a factor of 0.96.

3. Result

In FY2020, I systematically studied on-surface intermolecular coupling reaction of alkynes. This molecular system is explored by the combination of STM/STS and DFT calculations. More importantly, the tip-enhanced Raman spectroscopy (TERS)

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technique has been successfully integrated into my study in the past fiscal year, and it was used to experimentally judge the core chemical groups involved in the reaction intermediates or products at the single-chemical-bond level based on the corresponding vibrational modes.

Highly unsaturated π -rich carbon skeletons are versatile in tuning the structural and optoelectronic properties of low-dimensional carbon nanostructures. However, precise chemical identification and controllable integration of the target sp -/ sp^2 -carbon skeletons during synthesis are challenging and elusive. In this study, the π -skeletons generated by the coupling of terminal alkynes were visualized and identified at the single chemical bond level both topographically and spectroscopically, and further bond control was demonstrated. By a combination of STM/STS and TERS techniques, we precisely revealed the generated sp - sp^2 -carbon skeletons in real space as evidenced by their characteristic topographies and localized electronic and vibrational properties. Furthermore, by applying voltage pulses from the STM tip to the target molecules, bond control is achieved resulting in the dehydrogenative transition. DFT calculations further validate that the lowest unoccupied molecular orbital derived densities and the CC stretching modes of sp -carbon are valuable in recognition of π -skeletons. This study shows the versatility of spectroscopic information in realizing single-chemical-bond determination in surface chemistry, which can shed light on chemical identification and bond control of extensive carbon-based nanostructures/nanomaterials, and open up opportunities for further property optimization.

4. Conclusion

In FY2020, I have been trying to combine the theoretical calculations with STM/STS and TERS

experiments to examine a variety of molecular behaviors and reaction pathways towards target nanostructures 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/self-assembly processes on the surfaces.

5. Schedule and prospect for the future

In FY2021, 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 FY2021 to finish the current project.