

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

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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. 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 FY2021, I systematically studied on-surface intermolecular coupling reaction of alkynes. We visualized and identified π -skeletons generated by the coupling of terminal alkynes at the single-chemical-bond level both topographically and

spectroscopically, and further demonstrated bond control by a combination of scanning tunneling microscopy/spectroscopy (STM/STS) and tip-enhanced Raman spectroscopy (TERS) techniques. We chose 4,4'-diethynyl-1,1'-biphenyl (DEBP) as the precursor (i.e., terminal alkyne). We precisely revealed the generated sp-sp²-carbon skeletons (enyne and cumulene) in real space as evidenced by their characteristic topographies and localized electronic and vibrational properties. Our results clarify the occurrence of an addition reaction (i.e., non-dehydrogenative coupling) in generation of both connections on Ag(111). Furthermore, we show that applying voltage pulses from the STM tip to the target molecules provides bond control, resulting in the dehydrogenation in enyne connections. Density functional theory (DFT) calculations further validate that the lowest unoccupied molecular orbital (LUMO)-derived densities and CC stretching modes of sp-carbon assist recognition of π -skeletons.

Calculated LUMO of planar cumulene and enyne dimers in the gas phase.

To distinguish between these two connections formed by coupling of terminal alkynes (i.e., EN and CU indicated by red and blue arrows in Figure 1a, respectively), we performed DFT calculations. For simplicity, dimer structures were optimized on Ag(111), as shown in the right panels of Figure 1b and 1c. The results confirm that EN and CU connections can be attributed to enyne and cumulene, respectively. The calculated offsets in EN and CU connections (indicated in the structural models) are 1.12 and 3.15 Å, respectively, in good agreement with the experimental results (1.2 ± 0.1 and 3.3 ± 0.2 Å, respectively). Moreover, the enyne dimer adsorbed on Ag(111) is calculated to be more stable than the cumulene dimer by 0.11 eV, in line with the experimental observations that enyne serves as a dominant species. The simulated STM images based on the two structural models are shown in the left panels of Figure 1b and 1c, respectively. In the cumulene connection (with three consecutive double bonds), three central lobes are aligned with similar intervals. In contrast, in the enyne connection (with a double-single-triple conjugation) there is a triangular arrangement of the three lobes. Such electronic features resemble the calculated LUMO densities of the free dimers (Figure 1f and 1g). To examine these features more clearly, we performed STM measurements on the isolated dimers on Ag(110), where the dispersed distribution of DEBP, EN and CU dimers allows direct exploration of single species. Constant height scans of two dimers (Figure 1d and 1e) nicely resolved the characteristic orbital lobes and nodes. Interestingly, LUMO-derived electronic features unambiguously show the orientation of the C(sp²)-H (σ_{CH}) lobes at the centers, which results from the bonding combination of two LUMO orbitals of DEBP molecules. Furthermore, we synthesized 1,3-enyne *ex situ* and deposited it onto Ag(111), and found it has similar morphology to the

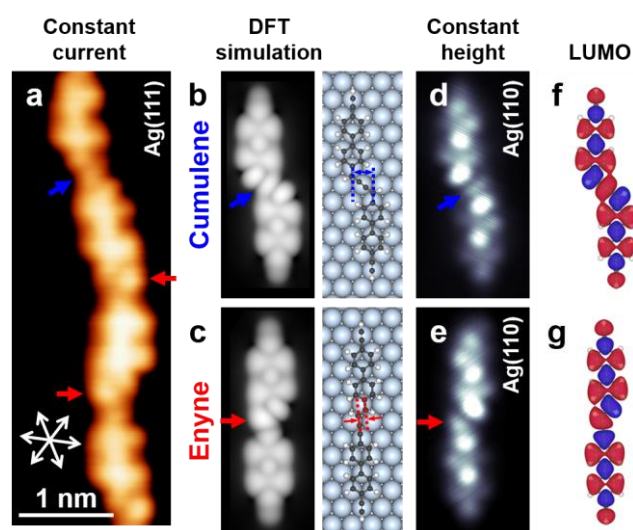


Figure 1. (a) Constant current STM images showing two kinds of connections within a chain obtained with a DEBP-functionalized tip. (b) and (c) Simulated STM images of cumulene and enyne dimers (left panels) based on the corresponding structural models on Ag(111) (right). (d) and (e) Constant height STM images of individual cumulene and enyne dimers on Ag(110) obtained with a DEBP-functionalized tip, respectively. (f) and (g)

in-situ one. The presence of the σ_{CH} features together with the ex-situ comparison supports the occurrence of addition reaction in the formation of both connections, and our tentative assignment of the new carbon skeletons to enyne and cumulene. By STM-TERS measurements, we then utilized the CC stretching modes of sp-carbon as Raman-active tags in the silent region to locate the enyne $C\equiv C$ and cumulene $C=C$ sp-carbon bonds, which further corroborated the scenario discussed above.

4. Conclusion

In conclusion, a thermal-induced on-surface synthesis strategy was applied to trigger the addition reaction constructing hybrid sp-sp²-carbon skeletons (i.e., enynes and cumulenes). The combination of STM/STS and TERS affords characterization of submolecular topographies and, more importantly, detection of characteristic electronic and vibrational features involved, which leads to precise chemical identification. It thus assists the discrimination of reaction schemes involved, and a non-dehydrogenative direct addition reaction scenario is revealed in the coupling of terminal alkynes on Ag(111).

5. Schedule and prospect for the future

In FY2022, 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 FY2022.

Usage Report for Fiscal Year 2021

Fiscal Year 2021 List of Publications Resulting from the Use of the supercomputer

[Paper accepted by a journal]

Chi Zhang, Rafael B. Jacubia, Yusuke Tanaka, Emiko Kazuma, Hiroshi Imada, Norihiko Hayazawa, Atsuya Muranaka, Masanobu Uchiyama, and Yousoo Kim, "Chemical identification and bond control of π -skeletons in a coupling reaction" *J. Am. Chem. Soc.*, 143, 9461 (June, 2021)