

**4th – 5th of March 2024**

**Okazaki Conference Center**

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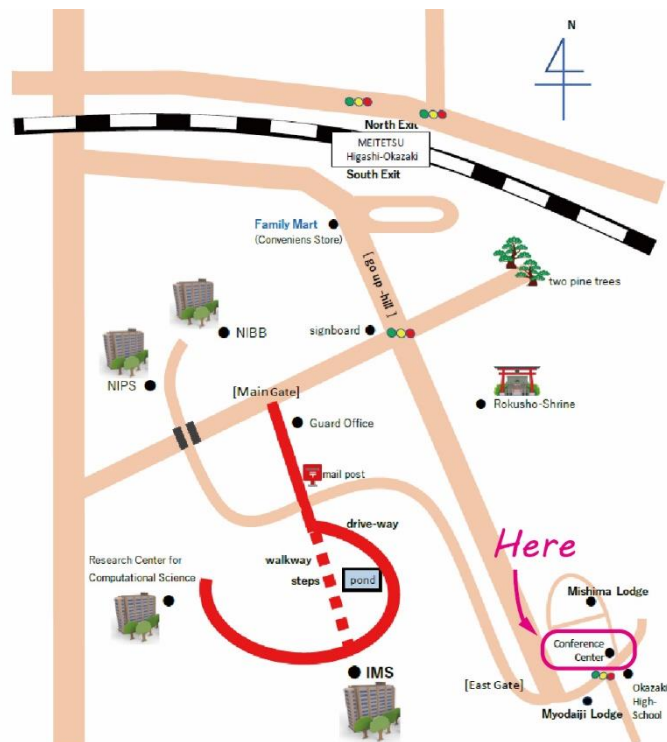
Quantum Design Japan

## Access to Okazaki Conference Center

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From Meitetsu Higashi-Okazaki station



## Venue Guide

- The talk session is held in **Ohsumi Hall**.
- The poster session is held in **Conference Room B/Foyer b**
- The Opinion Exchange Event is held in **Conference Room B**
- Luncheon seminar is held in:

**Conference Room B (Quantum Design Japan) and C (UNISOKU)**



## Day 1 (March 4th)

12:00-	Registration
13:00-13:05	Opening remarks
13:05-14:05	<b>Martin Wolf</b> (Plenary Lecture) <i>Ultrafast light-matter interaction probed in momentum and real space</i>
14:05-14:35	<b>Masahiro Shibuta</b> (Invited talk) <i>Ultrafast Spatial and Temporal Evolutions of Photoexcited Electrons at Functional Organic Surfaces and Interfaces</i>
14:35-14:50	Break
14:50-15:20	<b>Satoshi Kera</b> (Invited talk) <i>Many body effects define the material properties of molecular solids</i>
15:20-15:50	<b>Masaki Hada</b> (Invited talk) <i>Atomic or molecular motions in solids observed by ultrafast time-resolved electron diffraction</i>
15:50-16:20	<b>Masanori Sakamoto</b> (Invited talk) <i>Chemical energy conversion process using infrared light</i>
16:20-16:30	Break
16:30-17:00	<b>Yasumitsu Miyata</b> (Invited talk) <i>In-plane heterostructures based on 2D transition metal dichalcogenides</i>
17:00-17:20	<b>Yuki Tsujikawa</b> (Contributed Talk) <i>Study of a novel copper boride surface on Cu(110) with a one-dimensional quasi-periodic growth</i>
17:20-17:40	<b>Hiroaki Ooe</b> (Contributed talk) <i>Lattice-conserved polymerization of self assembled Br<sub>2</sub>-HPB molecules on Au(111)</i>
17:40-18:00	<b>Can Liu</b> (Contributed Talk) <i>Diffusion and adsorbate-adsorbate interaction of methoxy intermediates adsorbed on Ti sites of a Pt/TiO<sub>2</sub>(110) surface</i>
18:00-19:30	Poster session
19:30-21:00	Opinion Exchange Event

## Day 2 (March 5th)

- 8:50-9:20      **Yasuo Seto** (Invited talk)  
*Development of latent fingerprint detection by synchrotron soft X-ray microimaging*
- 9:20-9:50      **Masato Kotsugi** (Invited talk)  
*Feature extended Landau free energy model: extracting hidden information from magnetic domain image*
- 9:50-10:20     **Kiyohiro Adachi** (Invited talk)  
*Multi-scale structure analysis of white smoker chimney collected from the Mariana Trench using multiple synchrotron radiation techniques*
- 10:20-10:40    **Wang Zi** (Contributed Talk)  
*In situ soft-X-ray absorption spectroscopy study of photoexcited hole transfer in the cocatalyst-loaded SrTiO<sub>3</sub>:Al photocatalyst under UV irradiation*
- 10:40-11:00    Break
- 11:00-11:30    **Noriyuki Kodera** (Invited talk)  
*Video imaging of biological molecules in action by high-speed AFM*
- 11:30-12:00    **Kyoung-Duck Park** (Invited talk)  
*Tip-induced control of strong quantum light-matter interactions at the nanoscale*
- 12:00-12:30    **Chi Chen** (Invited talk)  
*Near-field Spectroscopic Imaging of Mesoscopic Photophysics: 2D Semiconductors and Lipid Bilayers*
- 12:30-13:30    Lunch (Luncheon seminar by UNISOKU and QDJ)
- 13:30-14:00    **Miyabi Imai** (Invited talk)  
*Atomic-scale visualization of single-molecule photocurrent channels by Photon-STM*
- 14:00-14:30    **Valeria Sheina** (Invited talk)  
*Atom by atom Electron spin resonance: coherence of Ti spins on ultra-thin MgO layers*
- 14:30-15:00    **Chun-Liang Lin** (Invited talk)  
*Tomography Scan of Charge Density Wave in NbSe<sub>2</sub>*
- 15:00-15:20    **Shota Takahashi** (Contributed talk)  
*Pioneering tip-enhanced nonlinear optics and spectroscopy*
- 15:20-15:30    Closing remarks
- 15:50-          Lab tour at IMS

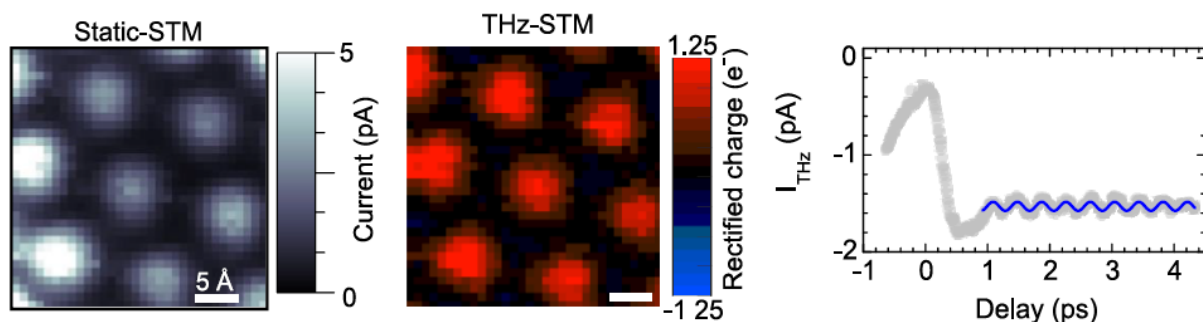
## Ultrafast light-matter interaction probed in momentum and real space

**Martin Wolf\****Fritz Haber Institute of the Max Planck Society, Faradayweg 4-6, 14195 Berlin, Germany*

Interaction of quantum matter with ultrashort light pulses may lead to emergent phenomena away from equilibrium. Examples are light harvesting in molecular semiconductors, exciton fission or ultrafast phase transitions in solids. Ultrafast laser spectroscopy provides a rich toolbox to study non-equilibrium dynamics of the underlying elementary excitations in the time-domain, but typically lacks spatial resolution. In order to obtain a complete picture of complex spatial-temporal dynamics of quantum matter, nanoscale spectro-microscopy should be combined with ultrafast temporal resolution. In this talk, I will discuss several complementary approaches to study the dynamics of elementary excitations from a momentum and real space perspective.

Recent advances in time-resolved photoemission spectroscopy (trARPES) combined with momentum space microscopy allow direct probing of excited states throughout the complete Brillouin zone. 2D materials and their heterostructures provide a vast playground to obtain a mechanistic understanding of exciton dynamics and probing the spatial extend of excitons in momentum-space. We also investigate the primary step of singlet fission in crystalline pentacene using orbital tomography and decompose energetically overlapping states on the basis of their orbital character. Our results show a charge-transfer mediated mechanism with hybridization of Frenkel and charge transfer states for fission of the singlet exciton [1].

Ultrafast scanning tunneling microscopy (STM) pushes spatial resolution to atomic scales. THz-lightwave-driven STM (THz-STM) and photon-assisted STM (ph-STM) are two approaches to probe the dynamics of charge, orbital and lattice degrees of freedom at the atomic scale [2]. While THz-STM uses single-cycle THz pulses to drive tunneling via classical rectification, ph-STM is based on photon absorption-induced tunneling. Here we use ph-STM to probe coherent phonons in ultrathin ZnO/Ag(111) via their coupling to an electronic resonance that enhances photon-assisted tunneling [3]. On the other hand, we can study the charge density wave (CDW) phase in 1T-TaS<sub>2</sub> using THz-STM, and probe locally the photoinduced Mott collapse and the coherent CDW amplitude motion (see Figure 1). Our results demonstrate the ability of ultrafast STM to reveal inhomogeneous non-equilibrium dynamics at atomic scales, previously obscured in spatially-averaged spectroscopy.



**Fig. 1.** Left: Charge density wave in TaS<sub>2</sub> imaged in constant height STM and THz-STM image of the same area ( $V_{DC} = +50$  mV  $U_{THz} = 450$  mV). Right: Rectified THz current versus time delay acquired on top of a selected CDW cluster. The periodic oscillations ( $t > 1$  ps) arise from the CDW amplitude mode ( $V_{DC} = -100$  mV  $U_{THz} = 450$  mV).

**References**

- [1] A. Neef *et al.*, *Orbital-resolved observation of singlet fission*, Nature **616**, 275 (2023).
- [2] M. Müller, *Imaging surfaces at the space-time limit: New perspectives of time-resolved scanning tunneling microscopy for ultrafast surface science*, Prog. Surf. Sci. 100727 (2023)
- [3] S. Liu *et al.*, *Nanoscale Coherent Phonon Spectroscopy*, Science Advances **8**, eabq5682 (2022).

\* Acknowledgements: This work was performed in collaboration with A. Neef, S. Beaulieu, S. Dong, J. Maklar, T. Pincelli, P. Xian, L. Rettig, J. Pflaum, R. Ernstorfer and S. Liu, A. Hammud, I. Hamada, T. Kumagai and M. Müller

## Ultrafast Spatial and Temporal Evolutions of Photoexcited Electrons at Functional Organic Surfaces and Interfaces

**Masahiro Shibuta**

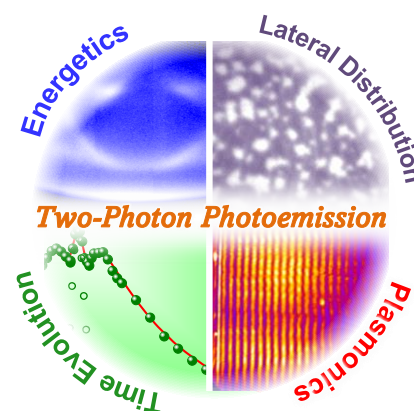
Department of Engineering, Osaka Metropolitan University, Japan

Understanding of the ultrafast electron dynamics at organic surfaces and interfaces is of high importance because it governs the functionalities of photoconversion devices. Since the growth of the organic layer exhibits inhomogeneity, time-resolved spectroscopy should be combined with microscopic way to observe the local phenomena. Two-photon photoemission spectroscopy (2P-PES) is a powerful method for studying the ultrafast electron dynamics, in which a first photon excites an electron in a targeted system and the excited electron is extracted by the aftercoming second photon. Using the optics for photoelectron emission microscopy as 2P-PEEM, the local excited-state dynamics can also be resolved with ~100 nm resolution [1].

On the fullerene C<sub>60</sub> layer, our 2P-PES and 2P-PEEM characterized the ultrafast dynamics of photocarrier generation in the C<sub>60</sub> layers with high energy, spatial, and temporal resolutions [1,2]. In addition, momentum-resolved 2P-PES showed a variety of highly-dispersive conduction bands in a well-assembled C<sub>60</sub> film; the nearly free-electron-like character originates from the diffuse superatomic molecular orbitals of C<sub>60</sub> [3].

In case of the pentacene layer, 2P-PEEM reflects the lateral distribution of excitons confined in the nanocrystal anisotropically grown on a substrate. Importantly, time-resolved 2P-PEEM captured the evolution of hot electrons dissipated into the substrate in 1 ps or sub  $\mu\text{m}$  ranges [4].

We have also demonstrated that 2P-PES and 2P-PEEM are valuable to observe plasmonic phenomena, which enhance the functionalities of organic system. By depositing atomically size-selected silver nanoclusters on C<sub>60</sub> layer, 2P-photoemission was drastically enhanced by plasmon-induced hot electrons [5]. Using a plasmon-active gold (Au) substrate for C<sub>60</sub> deposition, we clearly visualized and evaluated the propagating surface plasmon polaritons (SPPs) generated at the C<sub>60</sub>/Au interface [6]. These spectroscopic and microscopic methodologies probing 2P-photoemission have high potential to reveal the optical and plasmonic properties of various functional nanoscale systems.



### References

- [1] M. Shibuta, A. Nakajima, *J. Phys. Chem. Lett.* **14**, 3285-3295 (2023).
- [2] M. Shibuta *et al.*, *Sci. Rep.* **6**, 35853 (2016)., *Appl. Phys. Lett.* **109**, 203111 (2016).
- [3] M. Shibuta *et al.*, *J. Phys. Chem. C* **124**, 734 (2020)
- [4] M. Shibuta *et al.*, *in revision*
- [5] M. Shibuta, *et al.*, *ACS Nano* **15**, 1199 (2021).
- [6] M. Shibuta, *et al.*, *ACS Nano* **14**, 2044 (2020).



Many body effects define the material properties of molecular solids

**Satoshi Kera**

Institute for Molecular Science

Understanding the impacts of weak electronic interaction on the electron delocalization is required to discuss the rich functionalities of organic molecular materials. Moreover, the temporal and spatial effects of the strong coupling of phonon (collective lattice vibration) and/or local molecular vibration to electron must be unveiled. Angle-resolved ultraviolet photoelectron spectroscopy (ARUPS) is known to be a powerful technique to study the valence electronic structure. The frontier orbital of HOMO state can offer a wide variety of key information, that is essential to comprehend charge-hopping transport (small-polaron related transport) in the ordered monolayer film [1] as well as to coherent band transport in the molecular single crystal [2,3]. However, the experimental study of ARUPS fine features of the HOMO state has not been progressed till recently due to difficulty in the sample preparation, charging effects, irradiation damages, and so on [4,5]. We present the latest development for the ARUPS measurements of electronic states for rubrene ( $C_{42}H_{28}$ ) single crystal by using low-energy excited and high-resolution experimental station at BL7U of UVSOR synchrotron facility. We demonstrate how the HOMO band is observed differently against the previous results in theory [6] for the orthorhombic crystal structure of rubrene. To understand the effects of polaron formation on the electronic structure, a partially dressed polaron model that accounts for the electron–phonon interaction with frequency-dependent coupling constants based on Debye relaxation was proposed recently [7]. The precise experiments of the temperature dependence and 2D momentum-energy scanning for the ARUPS shed light on the problem of describing the characteristics of the electronic structure of organic materials, and thus the results would provide a perspective for the design of organic semiconductor devices.

#### References

- [1] S. Kera et. al., Prog. Surf. Sci., 84, 135 (2009).
- [2] N. Ueno et. al., Prog. Surf. Sci., 83, 135 (2008).
- [3] Y. Nakayama et. al., J. Mater. Chem. C., 8, 9090 (2020).
- [4] S. Machida et. al., Phys. Rev. Lett. 104, 156401 (2010).
- [5] F. Bussolotti et. al., Nat. Comm, 8, 173 (2017).
- [6] Y. Li et. al., J. Phys. Chem. Lett. 3, 3325 (2012).
- [7] H. Sato et. al., Nat. Mater. 21, 910 (2022).

Atomic or molecular motions in solids observed  
by ultrafast time-resolved electron diffraction

**Masaki Hada**

University of Tsukuba

In the last two decades, methods have been developed to directly observe the light-driven atomic and molecular motions of materials in real time. This progress is currently being made in elucidating the mechanisms of photoreactions or photoinduced phase transition phenomena in molecules or materials. [1,2]. These methodologies generally have a time resolution of  $10^{-14}$  to  $10^{-12}$  seconds (10 femtoseconds to 1 picosecond) and are called ultrafast measurements. Among the ultrafast measurement techniques, I will discuss ultrafast time-resolved electron diffraction measurements on solid-state materials in this presentation. Ultrafast time-resolved electron diffraction uses techniques like ultrafast time-resolved x-ray diffraction to measure the photoinduced changes of atomic or molecular coordinates.

The presentation shows the recent combined investigation of ultrafast time-resolved electron diffraction measurements, ultrafast transient absorption measurements, and first-principles calculations on a one-dimensional van der Waals heterostructure. The heterostructure contains carbon nanotubes (CNTs) as an inner core and boron nitride nanotubes (BNNTs) as an outer core. We found peculiar charge transfer channels between CNTs and BNNTs through the heterostructures.

#### References

- [1] S. Koshihara, T. Ishikawa, Y. Okimoto, K. Onda, R. Fukaya, M. Hada, Y. Hayashi, S. Ishihata, T. Luty, *Physics Reports* **942**, 1–61 (2022).
- [2] M. Hada, Y. Nishina, T. Kato, *Accounts of Chemical Research* **54**, 731–743 (2021).

## Chemical energy conversion process using infrared light

**Masanori Sakamoto**

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Solar radiation is the most abundant renewable energy source; however, its overall utilization remains inefficient as half of the energy is in the form of infrared (IR) light, which cannot be harnessed due to its low energy.

The presenter has been investigated the materials and method for converting the infrared light, an unused renewable energy source, into an energy resource. Localized surface plasmon resonance (LSPR) band can be tuned over a wide spectral range enabling solar energy utilization from ultraviolet (UV) to infrared (IR) regions. This excellent light-harvesting ability provide the technologies which convert wide range of light including IR region to chemical or electronic energies. However, the low conversion efficiency has been major drawbacks of LSPR-induced energy conversion.

LSPR materials of compound semiconductors, copper chalcogenide nanocrystals have shown unique carrier dynamics which demonstrate the efficient IR-responsive photocatalysts and device including IR sensor. The unique carrier transfer induced by LSPR excitation overcomes the limitation of low efficiency of plasmonic energy conversion realizing the efficient IR light to chemical energy conversion.

In this lecture, presenter will introduce the materials and mechanism of energy conversion of infrared light and applications for IR-responsive photocatalyst and devices.

**References**

- [1] M. Sakamoto\*, M. Hada\*, W. Ota, F. Uesugi, and T. Sato "Localised surface plasmon resonance inducing cooperative Jahn–Teller effect for crystal phase-change in a nanocrystal" *Nat. Commun.*, 2023, 14, 4471.
- [2] G. T. Mario, L. Zichao, C. Boiko, M. Sakamoto,\* A. Douhal\* "Hot Hole Transfer at Plasmonic Semiconductor/Semiconductor Interface" *Nanoscale*, 2023,15, 657-666.
- [3] Z. Lian, and M. Sakamoto\* et. al., "Harnessing infrared solar energy with plasmonic energy upconversion" *Nat. Sustain*, 2022, 5, 1092–1099.
- [4] Z. Lian, and M. Sakamoto\* et. al., "Plasmonic p-n Junction for Infrared Light to Chemical Energy Conversion" *J. Am. Chem. Soc.* 2019, 141, 2446-2450.
- [5] Z. Lian, and M. Sakamoto\* et. al., "Near infrared light induced plasmonic hole transfer at a nano-heterointerface" *Nat. Commun.* 2018, 9, 2314.

## In-plane heterostructures based on 2D transition metal dichalcogenides

**Yasumitsu Miyata**

Department of Physics, Tokyo Metropolitan University, Hachioji, Tokyo, Japan

Transition metal dichalcogenides (TMDs) are attractive materials with atomically-thin layered structures and unique physical properties. Recent advances in growth techniques have facilitated the fabrication of various TMD-based heterostructures. In particular, the edges of TMD single crystals can serve as platforms for the epitaxial growth of other TMDs. In this talk, we will present our recent progress in the chemical vapor deposition (CVD) and applications of such in-plane heterostructures (Figure 1) [1-5]. For example, two-step CVD process allows the formation of in-plane heterostructures with atomically sharp interfaces and nanometer-wide quantum wires [1,2,5]. In addition, tuning the precursor supply rates facilitates the realization of a compositionally graded TMD alloy [3,4]. We have demonstrated diverse functionalities of these heterostructures, including chiral or wavelength tunable electroluminescence [2,3], directional exciton energy transport [4], and band-to-band tunneling [5]. These TMD-based heterostructures would provide opportunities to investigate low-dimensional physics and explore applications in future devices.

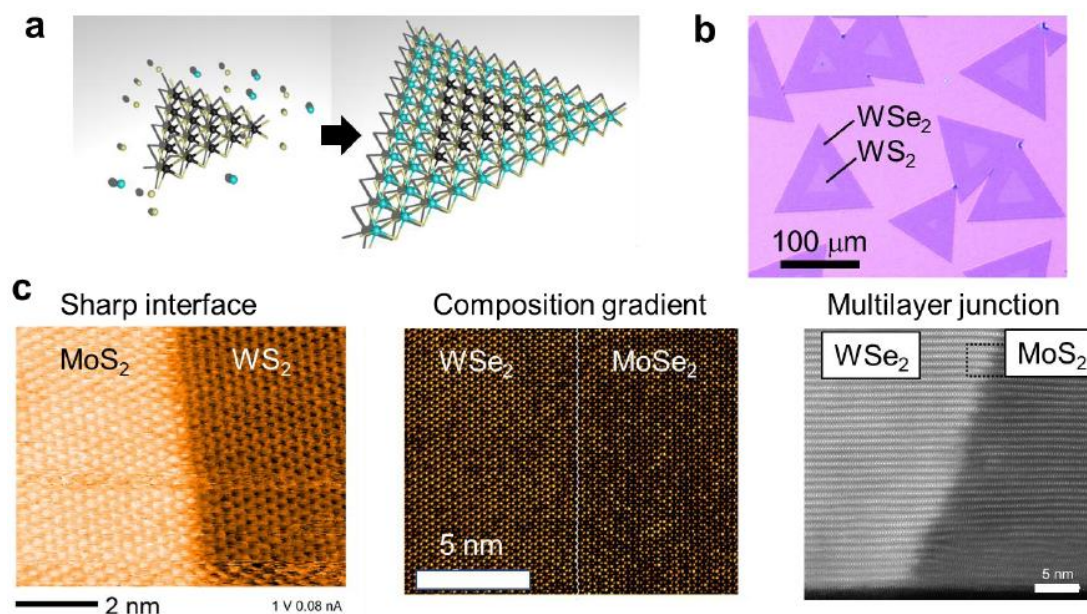


Figure 1 (a) Schematic illustrations of the heteroepitaxial growth of TMD in-plane heterostructure. (b) Optical images of WSe<sub>2</sub>/WS<sub>2</sub> in-plane heterostructures. (c) Examples of various TMD-based in-plane heterostructures.

## References

- [1] Y. Kobayashi, et al., ACS Nano, 13 (2019) 7527.
- [2] N. Wada, et al., Adv. Func. Mater., 32 (2022) 2203602.
- [3] J. Pu, et al., Adv. Mater. 34 (2022) 2203250.
- [4] M. Shimasaki, et al., ACS Nano, 16 (2022) 8205.
- [5] H. Ogura, et al., ACS Nano 17 (2023) 6545.

## Study of a novel copper boride surface on Cu(110) with a one-dimensional quasi-periodic growth

**Yuki Tsujikawa**<sup>A</sup>, Xiaoni Zhang<sup>A</sup>, Kazuki Yamaguchi<sup>A</sup>, Masahiro Haze<sup>A</sup>, Takeru Nakashima<sup>B</sup>, Arpita Varadwaj<sup>C</sup>, Yusuke Sato<sup>A</sup>, Masafumi Horio<sup>A</sup>, Yukio Hasegawa<sup>A</sup>, Fumio Komori<sup>A</sup>, Masaki Oshikawa<sup>A</sup>, Masato Kotsugi<sup>C</sup>, Yasunobu Ando<sup>B</sup>, Takahiro Kondo<sup>D</sup>, and Iwao Matsuda<sup>A</sup>

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A new surface compound material, copper boride (Cu-boride), has recently been achieved in a two-dimensional (2D) form on the Cu(111) surface [1-4]. Compounds with this combination of elements were previously not known to synthesize in a 3D bulk form due to the small difference in electronegativities and large difference in atomic sizes. However, it was found to exist in a 2D form, exhibiting a unique 1D boron chain configuration combined with the Cu atoms. The combination of molecular orbitals of boron chains and hybridization with Cu enables the synthesis of this exotic compound.

Here, we report a new Cu-boride surface synthesized on the anisotropic Cu(110) substrate [5]. The B/Cu(110) surface displayed 1D growth, with atomic chains periodically aligned parallel to one another. The chains grew in a self-assembled manner, extending over hundreds of nanometers, even crossing the surface steps. Intriguingly, the 1D structure of the chains showed no average lattice, resulting in a quasi-periodic order of two lengths, verified through Fourier transform analysis. The observed long-range formation of a quasi-periodic 1-D structure was theoretically modeled under a 1-D quasi-crystal condition, and the predicted conditions aligned with the structural parameters determined experimentally. This quasi-periodic 1-D copper boride system serves as a unique platform for studying 1-D quasi-crystallinity in an actual material, ensuring the rich nature of structures and bindings in the boron system [6].

### References

- [1] Y. Tsujikawa *et al.*, Physical Review B 106, 205406 (2022).
- [2] C. Yue *et al.*, Fundamental Research 1, 482 (2021).
- [3] X.-J. Weng *et al.*, Physical Review Materials 4, 074010 (2020).
- [4] Y. Tsujikawa *et al.*, e-Journal of Surface Science and Nanotechnology, Advance online publication, <https://doi.org/10.1380/ejssnt.2023-058>
- [5] Y. Tsujikawa *et al.*, Surface Science **732**, 122282 (2023).
- [6] Y. Tsujikawa *et al.*, Nano letters, accepted

Lattice-conserved polymerization of self-assembled Br<sub>2</sub>-HPB molecules on Au(111)

Hiroaki OOE and Takashi YOKOYAMA

Yokohama City University

The bottom-up construction of covalent nanostructures has been achieved through on-surface polymerization of tailor-made precursors.<sup>[1]</sup> Recently, the influence of precursor self-assembly on the on-surface polymerization reactions has also been reported. The polymerization of self-assembled precursor molecules has been generally understood as that the restricted molecular diffusion leads to the formation of covalent bonding between closely adjacent reaction sites.<sup>[2]</sup> Nevertheless, the detailed influence of self-assembled structure has not been clear.

In this study, we focus upon the influence of self-assembly on the polymerization reaction. As a reaction precursor, dibromo-substituted hexaphenylbenzene (Br<sub>2</sub>-HPB; Figure 1) is used. In our previous report, as well as the Br<sub>2</sub>-HPB precursors, covalently bonded HPB polymer chains produced by the on-surface polymerization also exhibited a long-range ordering on Au(111), as shown in Figure 2a and 2b.<sup>[3]</sup> This indicates that, during the polymerization process, the ordered self-assembly has been maintained apparently. Nevertheless, the structural disordering is expected by the sequential polymerization reactions due to the molecular size difference between Br<sub>2</sub>-HPB precursor and HPB polymer. To clarify why the ordered self-assembly has been maintained, we have investigated the partially polymerized mixture phase, which is achieved by short annealing.

After the short annealing at 200 °C, we have observed a well-ordered structure composed of both Br<sub>2</sub>-HPB precursors and HPB polymers. The ordered mixture phase suggests that the polymerization of Br<sub>2</sub>-HPB proceeds without the disruption of ordered self-assembly. From the detailed analysis of the mixture phase, we find that the polymerization of Br<sub>2</sub>-HPB is accompanied by the molecular rotation to conserve the self-assembled array of Br<sub>2</sub>-HPB. After higher temperature annealing at 400 °C, the finally produced hexabenzocoronene (HBC) nanographene chains show a tendency to align their orientation, as shown in Figure 2c. This orientation alignment should be attributed to the ordered structure of HPB polymers. Thus, we have clarified that the self-assembled ordering of Br<sub>2</sub>-HPB precursor molecules influences on the molecular arrangements not only after the polymerization process but also even after the cyclodehydrogenation process.

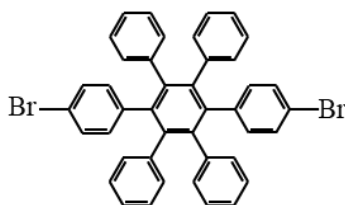


Fig. 1. Chemical structure of Br<sub>2</sub>-HPB molecule.

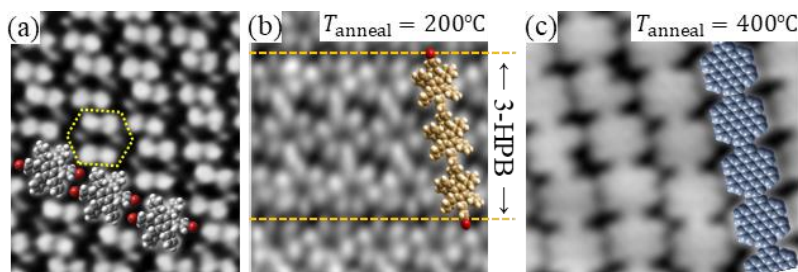


Fig. 2. LT-STM images of (a) self-assembled Br<sub>2</sub>-HPB precursors, (b) self-assembled HPB polymers, and (c) HBC nanographene chains.

## References

- [1] C. Cai et al., *Nature*, 466 (2010) 470. [2] J. Huang et al., *ACS NANO* 15 (2021) 4617.  
 [3] H. Ooe, K. Ikeda, and T. Yokoyama, *J. Phys. Chem. C*, 127 (2023) 7659.

## Diffusion and adsorbate-adsorbate interaction of methoxy intermediates adsorbed on Ti sites of a Pt/TiO<sub>2</sub>(110) surface

**Can Liu**<sup>1</sup>, Bang Lu<sup>1</sup>, Hiroko Ariga Miwa<sup>2</sup>, Min Gao<sup>1</sup>, Jun-ya Hasegawa<sup>1</sup>, Ken-ichi Shimizu<sup>1</sup>, Kiyotaka Asakura<sup>1</sup>, Satoru Takakusagi<sup>1</sup>

<sup>1</sup>Hokkaido University, <sup>2</sup>The University of Electro-Communications

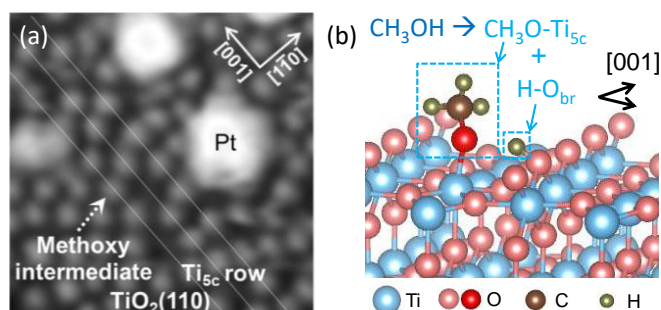
Understanding the dynamic behavior of intermediate adsorbates on a catalyst surface is crucial because it significantly influences the catalytic performance. We have recently reported that the thermal decomposition property of methoxy intermediates adsorbed on the Ti sites of a Pt/TiO<sub>2</sub>(110) surface was controlled by their diffusion and reverse spillover.<sup>1,2</sup> It has been well known that the mobility of the intermediate adsorbates is affected by the adsorbate-substrate and adsorbate-adsorbate interactions. In this study, we examined the diffusion mechanism and adsorbate-adsorbate interaction of the methoxy intermediates on the Pt/TiO<sub>2</sub>(110) surface by scanning tunneling microscopy (STM), density functional theory (DFT) calculation and space-correlation analysis.

Figure 1 shows a typical STM image of the Pt/TiO<sub>2</sub>(110) surface after exposure to methanol vapor at room temperature. The methoxy adsorbates were present on the Ti<sub>5c</sub> sites of the TiO<sub>2</sub>(110) after they were created on the Pt nanoparticles and then spilled over to the TiO<sub>2</sub> surface. The saturation coverage of the methoxy intermediates was 0.14 ML (1ML= 5.2×10<sup>18</sup>

/m<sup>2</sup>). Sequential STM imaging showed that, the methoxy adsorbates were mobile at room temperature and diffused both along the [001] and [1 $\bar{1}$ 0] directions. DFT calculations of a single methoxy adsorbate on a TiO<sub>2</sub>(110) surface showed that the conversion to methanol-like intermediate is a key for facile diffusion on the TiO<sub>2</sub>(110) surface. Along the [001] direction, the methanol-like intermediate diffuses to the nearest Ti<sub>5c</sub> site with an energy barrier of 0.68 eV. Along the [1 $\bar{1}$ 0] direction, the barrier could be lowered to 0.64 eV with the presence of an additional HO<sub>br</sub>. The collective behavior of the methoxy species was also studied by space correlation analysis. The neighboring distance between the two methoxy adsorbates along the [001] direction was more than 3 lattice constants, indicating a repulsive interaction between them which may limit the saturation coverage of the methoxy intermediates and act as a driving force for their diffusion along the [001] direction.

### References

- [1] S. Takakusagi, K.-i. Fukui, R. Tero, K. Asakura, Y. Iwasawa, *Langmuir* **2010**, *26*, 16392.  
 [2] C. Liu, B. Lu, H. Ariga-Miwa, S. Ogura, T. Ozawa, K. Fukutani, M. Gao, J.-y. Hasegawa, K.-i. Shimizu, K. Asakura, S. Takakusagi, *J. Am. Chem. Soc.* **2023**, *145*, 19953.



**Figure 1.** (a) STM image (7.4×7.4 nm<sup>2</sup>) of the Pt/TiO<sub>2</sub>(110) surface after exposure to 5 L methanol vapor. (b) Atomic model of methoxy adsorbate adsorbed at the Ti<sub>5c</sub> site.

Development of latent fingerprint detection by synchrotron soft X-ray microimaging

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Takuo Ohkochi<sup>BAC</sup>, Masaki Oura<sup>A</sup>

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Fingerprint (FP) examination is key forensic technology. FP is composed of secretion of sweat and sebaceous glands, as well as contaminations which were adhesive to the fingers. Inclusions of FP are water, organic compounds such as amino acids, proteins, carbohydrates, organic acid, fatty acids and lipids, inorganic compounds such as alkali metals and halogens, and also contaminants such as cosmetics. Matching of ridge pattern taken from latent FP left on crime scene surface with those of reference FP, leads to personal identification, like forensic DNA typing. Analysis of FP components provide personal information and history; age, gender, body status, time between fingerprint adhesion and sampling, and special action such as handling of explosives. Many FP detection and enhancement methods have been used in real criminal investigation, such as ninhydrin method and cyanoacrylate method. Fourier-transform infra-red (FT/IR) spectroscopy, mass spectrometry and electrochemical method are also developed. However, it is difficult to get ridge pattern from unclear latent FP. Especially, in fire scenes FPs are severely deteriorated by heating, which cause FP visualization impossible. In this research, synchrotron soft X-ray microimaging technique was compared with conventional optical microscopy, FT/IR microimaging and scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX). for visualizing heated FP.

Index fingers were pushed on various substrates (silicone, glass, stainless steel, aluminum, brass) to form FPs, and sealed FPs were treated by heating (400°C for 3 h). Untreated and heated FPs were subject to scanning soft-X-ray fluorescent microscopy (SXFM) and photoemission electron microscopy (PEEM) at SPring-8 BL17SU, and also laboratory analysis. Untreated FPs showed images of assemblies of ridge streaks (several hundred  $\mu\text{m}$  width, about 1  $\mu\text{m}$  height) separated each other by few hundred  $\mu\text{m}$  under optical microscopy observation, but after heating, FP ridge pattern could not be clearly observed. Micro FT/IR spectroscopy showed spectrum composed of absorption peaks derived from sweat and sebaceous gland inclusion for untreated FPs, but after heating, characteristic IR absorption could not be observed. By SEM-EDX measurement, clear FP ridge patterns could not be observed for heated FPs, but aggregates of about 1  $\mu\text{m}$  NaCl particles were observed on silicone substrate. SXFM (0.5  $\mu\text{m}$  size, photon energy 2 keV, 40  $\mu\text{m}$  step scanning) clearly visualized FP ridge streaks on all the substrates for untreated FPs by observing Na  $K\alpha$ , O  $K\alpha$  and elastic peaks, but for heated FPs, SXFM visualized FP ridge streaks only on silicone, stainless steel and brass substrates by detecting Na  $K\alpha$  peak. PEEM successfully visualized positive particles which formed FP ridge streaks at Na K-edge for heated FPs on all the substrates, where in magnified field of view, about 1  $\mu\text{m}$ -size Na particles were observed.



Feature extended Landau free energy model: extracting hidden information from  
magnetic domain image

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Microscopic materials analysis is essential to achieve desirable performance in next-generation nanoelectronic devices, such as low power consumption and high speeds. However, the magnetic materials involved in such devices often exhibit incredibly complex interactions between nanostructures and magnetic domains. This, in turn, makes functional design challenging. Traditionally, researchers have performed a visual analysis of the microscopic image data. However, this often makes the interpretation of such data qualitative and highly subjective. What is lacking is a causal analysis of the mechanisms underlying the complex interactions in nanoscale magnetic materials.

We carried out in automating the interpretation of the microscopic image data. This was achieved using an “extended Landau free-energy model” that we developed using a combination of topology, data science, and free energy<sup>1-6</sup>. The model could illustrate the physical mechanism as well as the critical location of the magnetic effect, and proposed an optimal structure for a nano device. The model used physics-based features to draw energy landscapes in the information space, which could be applied to understand the complex interactions at the nanoscales in a wide variety of materials.

#### References

- [1] S. Kunii, K. Masuzawa, A. L. Foggiatto, C. Mitsumata & M. Kotsugi, *Sci. Rep.* 12, 19892 (2022)
- [2] A. L. Foggiatto, S. Kunii, C. Mitsumata & M. Kotsugi, *Communications Physics* 5, 277 (2022)
- [3] S. Kunii, A. L. Foggiatto, C. Mitsumata & M. Kotsugi, *Sci. Tech. and Adv. Mater. Methods*, 2 445-459 (2022)
- [4] C. Mitsumata, M. Kotsugi, *J. Magn. Soc. Jpn*, 46, (2022) pp. 90-96
- [5] K. Masuzawa, S. Kunii, A. Foggiatto, C. Mitsumata, M. Kotsugi, *T. Magn. Soc. Japan*. 6 (2022), 1-9.
- [6] T. Nishio, M. Yamamoto, T. Ohkochi, D. Nanasawa, A. Foggiatto, M. Kotsugi, *Sci. Tech. and Adv. Mater. Methods*, 2, pp 345-354, (2022)

Multi-scale structure analysis of white smoker chimney collected from the Mariana Trench using multiple synchrotron radiation techniques

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What is the origin of life? — This is a question that has long intrigued mankind. Microorganisms are engaged in chemosynthesis in deep-sea hydrothermal vents (HVs), which may hold the key to the elucidation of the origin of life. Scientists once believed that light was necessary for life. However, the discovery in 1979 of microorganisms swarming around deep-sea HVs changed the conventional wisdom. Following the discovery of Black Smoker HVs, a giant HV (White Smoker Chimney), which emitted alkaline pH hydrothermal water was discovered.

Remarkable progress in extreme environment science continues to expand the frontiers of science on the origin of life. However, studies on HVs have been conducted mainly from the viewpoints of microbiology and geology, and the structural order and function are unexplored issues.

We have been working to elucidate the structure and function of White Smoker Chimney from multiple perspectives using multiple synchrotron radiation techniques. White Smoker Chimney has a hierarchical structure, consisting of water channels (~100  $\mu\text{m}$ ), walls (~10  $\mu\text{m}$ ), nanochannels (nm-scale), and Brucite layers (sub nm-scale). The White Smoker Chimney sample was collected by Shinkai 6500 from the Mariana Trench. The orientation of Brucite layers and alignment of walls were analyzed by WAXS and SAXS using a focused X-ray beam at BL32XU and BL38B1, respectively. To reveal the function of Chimney in deep sea, the state of water inside the Chimney was further analyzed by IR and XAS at BL43IR and BL17SU, respectively. Further details on the experiments and results were explained in the presentation.

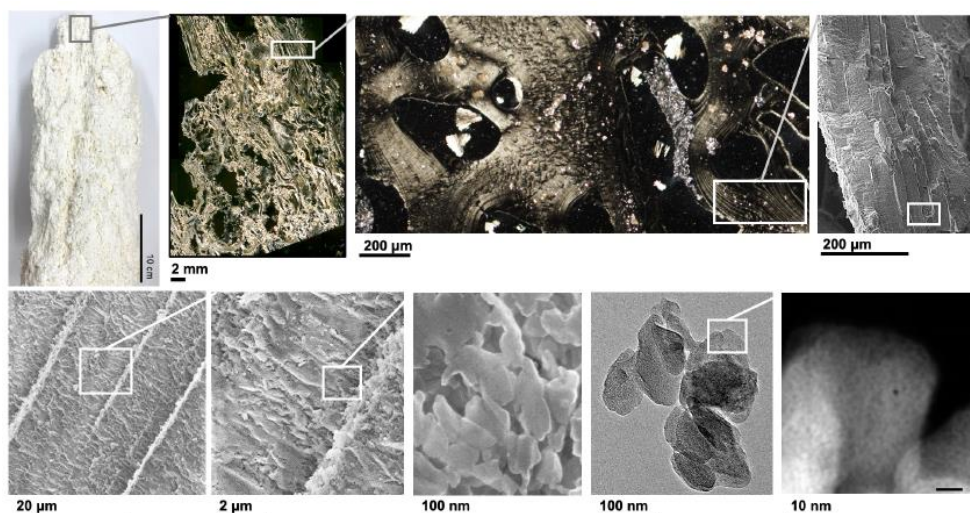


Figure1. Hierarchical structure of the White Smoker Chimney

#### References

[1] Lee H-E, Okumura T, Ooka H, Adachi K, et al. Osmotic Energy Conversion in Deep-Sea Hydrothermal Vents. ChemRxiv, (doi:10.26434/chemrxiv-2023-v9nc6).

*In situ* soft-X-ray absorption spectroscopy study of photoexcited hole transfer in the cocatalyst-loaded SrTiO<sub>3</sub>:Al photocatalyst under UV irradiation

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Photocatalytic water splitting is one promising way to providing clean hydrogen as energy source. Recently, Al doped SrTiO<sub>3</sub> (STO) with co-catalysts loading which Rh/Cr<sub>2</sub>O<sub>3</sub> as hydrogen evolution reaction (HER) site and CoOOH as oxygen evolution reaction (OER) site gives up to 96 per cent of quantum efficiency at a UV-light wavelength range [1]. During the photocatalytic water splitting reaction, photoexcited charge carriers transfer to the OER and HER co-catalysts have not been observed yet. In this work, the oxidation process of the Co-containing OER site is observed with *in situ* soft-X-ray absorption spectroscopy (SXAS) technique [2].

A newly modified cell using the conversion electron yield (CEY) mode was used to conduct *in situ* SXAS measurements at beamline 13A at the Photon Factory, with which UV-Vis lights can be delivered onto sample surfaces under ambient pressure conditions and surface-sensitive information on photoinduced chemical states changes of the co-catalysts are obtained. *In situ* Co-L SXAS measurements have been conducted for the STO photocatalyst with the both co-catalysts loaded. Under UV irradiation without water vapor (He flow only), the Co species in CoOOH was reduced as evidenced by increasing of Co<sup>2+</sup> component. However, when saturated water vapor was introduced, the Co<sup>2+</sup> component drastically diminished, showing oxidation from Co<sup>2+</sup> to Co<sup>3+</sup>, and the Co<sup>3+</sup> peak top further shifts to the higher energy side with UV irradiation time, which provides evidence for that UV-induced hole carriers transport to the Co species, and oxidize toward higher oxidation states. DFT simulations indicate photoexcited holes are not localized on a specific Co atom but tend to be gathering on the topmost surface layer of CoOOH. Interestingly, a STO photocatalyst with only CoOOH co-catalyst loaded (without HER site) exhibits no oxidation but reduction of Co, indicating that the HER site, thus, Rh/Cr<sub>2</sub>O<sub>3</sub>, is crucial to act as an electron sink to trap photoinduced electrons and promote efficient hole transfer to the CoOOH site to oxidize Co. We conclude that water atmosphere and the presence of HER site are essentially important for the photoinduced hole transfer to the CoOOH site and resultant oxidation of Co.

#### References

- [1] Takata, T. et al. Nature 581, 411–414 (2020).
- [2] Shimizu, H. et al Phys. Chem. Chem. Phys. 24, 2988–2996 (2022).

## Video imaging of biological molecules in action by high-speed AFM

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High-speed atomic force microscopy (high-speed AFM) is a unique microscopy that allows direct real-time visualization of biological macromolecules in action under near-physiological conditions, without any chemical labeling. Typically, the temporal resolution is sub-100 ms, and the spatial resolution is 2–3 nm in the lateral direction and ~0.1 nm in the vertical direction [1]. A wide range of biomolecular systems and their dynamic processes have been studied by high-speed AFM, providing deep mechanistic insights into how biomolecules function. Notably, high-speed AFM is particularly powerful in visualizing large and flexible biomolecular systems, which conventional structural biology methods are unable to visualize. These unique features of high-speed AFM are well demonstrated in recent research results that visualize the structural dynamics of intrinsically disordered regions, single polypeptide chains with height of ~0.5 nm in a protein (Fig. 1a) [2], the gathering of translation factors around the ribosomal stalk complex (Fig. 1b) [3], and the long-range DNA degradation of CRISPR-Cas3 driven by its helicase and nuclease activities (Fig. 1c) [4]. In the presentation, after overviewing the principles and performance of high-speed AFM, movies showing dynamic behaviors of biomolecules will be shown. In addition, our recent efforts to improve the speed performance of high-speed AFM will be discussed [5].

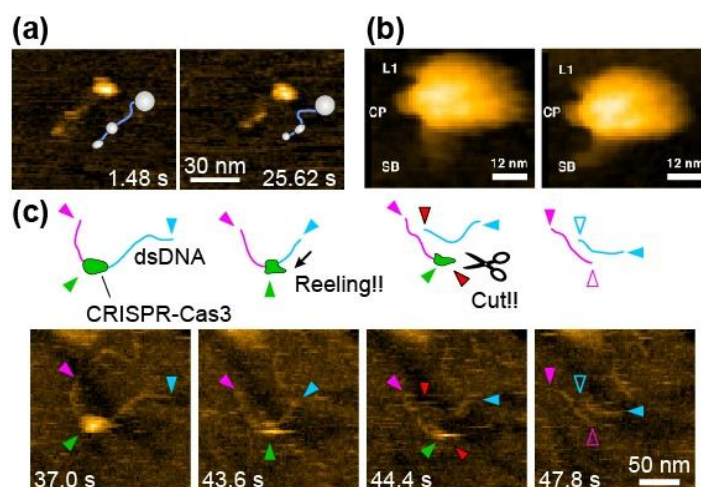


Fig. 1 Typical high-speed AFM images showing biomolecules in action. (a) An intrinsically disordered protein involved in chromatin remodeling. (b) Ribosomal stalk complex (SB) with two structural states. (c) DNA degradation by CRISPR-Cas3 enzyme.

## [References]

- [1] Ando, T.; Uchihashi, T.; Koderu, N., High-speed AFM and applications to biomolecular systems. *Annu. Rev. Biophys.* 2013, 42, 393-414.
- [2] Koderu, N.; Noshiro, D., Dora, S. K.; ...; Longhi, S.; Ando T., Structural and dynamics analysis of intrinsically disordered proteins by high-speed atomic force microscopy. *Nat. Nanotechnol.* 2021, 16, 181-189.
- [3] Imai, H.; Uchiumi, T.; Koderu, N., Direct visualization of translational GTPase factor pool formed around the archaeal ribosomal P-stalk by high-speed AFM. *PNAS* 2020, 117, 32386-32394.
- [4] Yoshimi, K.; Takeshita, K.; Koderu, N.; ...; Mashimo, T., Dynamic mechanisms of CRISPR interference by *Escherichia coli* CRISPR-Cas3. *Nat. Commun.* 2022, 13, 4917.
- [5] Umeda, K.; McArthur, S. J.; Koderu, N., Spatiotemporal resolution in high-speed atomic force microscopy for studying biological macromolecules in action. *Microscopy* 2023, 72, 151-161.

Tip-induced control of strong quantum light-matter interactions at the nanoscale

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The tunability of the bandgap, radiative emission, and energy transfer in transition metal dichalcogenide (TMD) monolayers provides a new class of functions for a wide range of ultrathin photonic devices. Additionally, understanding and controlling the nanoscale transport of excitonic quasiparticles, such as excitons and trions, in atomically thin 2D semiconductors are crucial to produce highly efficient nano-excitonic devices. In this work, we present a dynamic nano-mechanical strain-engineering of naturally-formed wrinkles in a  $WSe_2$  monolayer, with real-time investigation of nano-spectroscopic properties using tip-enhanced cavity-spectroscopy [1-4]. We reveal the modified nano-excitonic properties by the induced tensile strain at the wrinkle apex, exhibiting the exciton funneling phenomenon. In addition, we demonstrate a nanogap device to selectively confine excitons or trions of 2D TMDs at the nanoscale, facilitated by the drift-dominant exciton funneling into the strain-induced local spot. Furthermore, we present a method for the all-optical control of the exciton-to-trion conversion process and its spatial distributions in a  $MoS_2$  monolayer. We exploit propagating surface plasmon polaritons (SPPs) to localize hot electrons in a 2D TMD transferred on a metal-insulator-metal (MIM) waveguide. Our work provides a new strategy for robust, tunable, and ultracompact nano-excitonic devices using atomically thin semiconductors.

#### References

- [1] Yeonjeong Koo et al., *Advanced Materials* 33, 2008234 (2021).
- [2] Hyeongwoo Lee et al., *Advanced Functional Materials* 31, 2102893 (2021).
- [3] Hyeongwoo Lee et al., *Science Advances* 8, eabm5236 (2022).
- [4] Hyeongwoo Lee et al., *Nature Communications* 14, 1891 (2023).

Near-field Spectroscopic Imaging of Mesoscopic Photophysics:  
2D Semiconductors and Lipid Bilayers.

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Scanning near-field optical microscopy (SNOM) is a scanning probe technique that combines optics with atomic force microscopy (AFM) to achieve subdiffraction-limit optical resolution. We employed near-field photoluminescence (NF-PL) to study the atomically sharp 1D interfaces between WS<sub>2</sub> and MoS<sub>2</sub> [1]. With an optical resolution of 68 nm, a 105 nm-wide region for quenched PL was confirmed using NF-PL imaging, which resolved the narrowest quenching region thus far. For low-quantum-yield materials, we developed the near-field broadband transmission (NF-tr) method, which provides abbreviation-free and nanoscale-resolution imaging capabilities for the entire conduction band over a highly lateral inhomogeneity [2]. Both bandgap evolutions with varying compositions and bilayer coupling effects were visualized in real space with a spatial resolution of 135 nm.

With further instrumentation challenges [3], we developed a liquid-phase SNOM system for lateral distribution and phase segregation of supported lipid bilayers (SLB). Surprisingly, the SNOM tip can manipulate local lipid molecules from the gel phase to the fluid phase and vice versa, which causes the fluorescence contrast to flip the opposite. This demonstrates that there was no particular partition of the fluorescence tag in the fluid or gel phases. Our results reveal the fundamental mechanisms and offer a practical guide for interpreting the partitioning of fluorescent tags.

#### References

- [1] H.-C. Chou *et al.*, *Nanoscale* 14, 6323 (2022).
- [2] P.-W. Tang *et al.*, *ACS Nano*, 16, 5, 7503 (2022).
- [3] J.-R. Yu *et al.*, *Rev. Sci. Instrum.* 91, 073703 (2020).

## Atomic-scale visualization of single-molecule photocurrent channels by Photon-STM

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Photoinduced electron transfer (PET) from excited molecules plays central roles in various light energy conversion systems, and therefore it has been widely studied using optical spectroscopy and photocurrent measurement. To understand the detailed insights into PET, as an initial process of photocurrent generation, microscopic techniques for photocurrent measurement have been developed by combining scanning probe microscopes (SPMs) and optical systems. These techniques have allowed the efficiency of photocurrent generation to be correlated to local morphology of molecular films on the nanoscale, far below the diffraction limit of the light. However, the spatial resolution of these techniques is still not enough to distinguish individual molecules, and observed PET signals are often obscured by ensemble-averaging over inhomogeneous local structures. Since electron transfer between two substances depends on the direct overlap of their electron wavefunctions, atomic-scale geometric changes can profoundly affect the efficiency of this process. Consequently, it would be highly desirable to develop a photocurrent measurement technique with atomic spatial resolution that could reveal the fundamental physics governing the PET process.

In this study, we achieve atomic-scale visualization of photocurrent channels of a single free-base phthalocyanine (FBPc) molecule [1] using a scanning tunneling microscope (STM) combined with a narrow-width tunable laser (Figures a, b) [2-4]. PET from the single FBPc molecule in the first singlet excited state was clearly detected via the photoinduced tunneling current through the STM tip. Depending on the applied bias voltage, not only the direction but also the spatial distribution of the photocurrent changes remarkably. The atomically resolved photocurrent images allowed us to discover multiple counterflowing photocurrent channels even at a voltage where the averaged photocurrent is almost zero. Moreover, we found direct evidence of competition between PET and photoluminescence (PL), and demonstrated the controllability of their branching ratio during energy relaxation by positioning the STM tip with three-dimensional, atomic precision. Our findings present that specific photocurrent channels can be selectively promoted or suppressed by tuning the coupling between molecular orbitals and metal wavefunctions, which provides a new perspective for improving the energy conversion efficiency by atomic-scale electronic and geometric engineering of molecular interfaces.

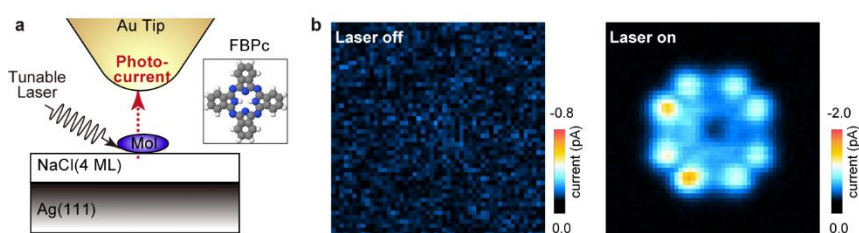


Figure: a, A schematic of the experiment and the structure of an FBPc.

b, The current images over the molecule measured in the laser-off (left) and laser-on (right) states ( $V_S = -2.0$  V,  $3.0$  nm  $\times$   $3.0$  nm).

## References

- [1] M. Imai-Imada et al., *Phys. Rev. B* **98**, 201403(R) (2018).
- [2] M. Imai-Imada et al., *Nature* **603**, 829 (2022).
- [3] H. Imada, M. Imai-Imada et al., *J. Chem. Phys.* **157**, 104302 (2022).
- [4] H. Imada, M. Imai-Imada et al., *Science* **373**, 95 (2021).

Atom by atom Electron spin resonance: coherence of Ti spins on ultra-thin MgO layers

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Scanning tunneling microscopy (STM) combined with electron spin resonance (ESR) enables a coherent control of atomic spins on surfaces. However, the two metallic electrodes, i.e., tip and substrate, and tunneling electrons, inducing scattering of the spins, significantly limits the coherence of their quantum states [1]. Recently, introduction of a 'remote' spin [2], which is free from the tunneling-induced scattering, has shown a coherence time ( $T_2$ ), reaching the theoretical limit as determined only by its spin relaxation time ( $T_1$ ) [3]. Here, we report an ESR-STM study on the spin relaxation and quantum coherence of single Ti atoms ( $S = 1/2$ ) on 2 and 3 ML MgO,  $Ti^{(2)}$  and  $Ti^{(3)}$ , respectively. First,  $Ti^{(3)}$  in the tunnel junction showed a  $T_2$  that is longer by the factor of  $\sim 5$  than  $Ti^{(2)}$ , indicative of a considerably suppressed coupling with the substrate on 3 ML. In addition, both  $Ti^{(2)}$  and  $Ti^{(3)}$  showed linear dependence of decoherence rates ( $1/T_2$ ) on the tunneling current, with the same slopes, which revealed the effect of the tunneling electron on the spin dynamics, contributing independent of the decoupling layer thickness, and thus allowed a quantitative understanding on it. A remote  $Ti^{(3)}$  showed  $T_1$  of  $\sim 10$  ns, longer by 2 orders of magnitude than  $Ti^{(2)}$ , which is well understood by the enhanced decoupling from the substrate. However,  $T_2$  of a remote  $Ti^{(3)}$  remained similar to that of  $Ti^{(2)}$ , implying existence of a significant decoherence process as revealed by free induction decay time ( $T_2^*$ ) measurement, probably due to the spin fluctuation of the single atom magnet in its proximity [4]. This work serves as a quantitative insight, pointing at the importance of decoupling the spins from the substrate as well as the tunneling electrons and shedding light on the on-surface spins as a noble atomic-scale qubit platform [3].

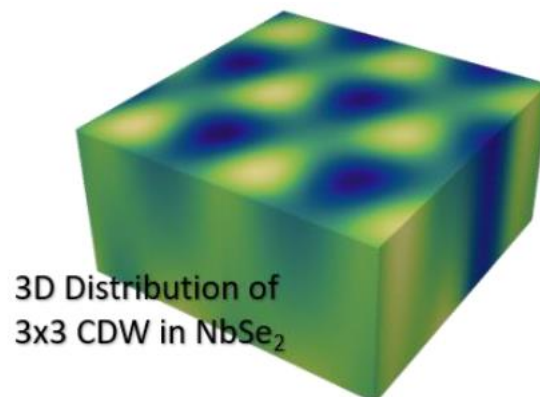
References:

- [1] W. Paul et al. *Nature Phys.* 13, 403–407 (2017).
- [2] S. Phark et al. *ACS Nano* 17, 14144–14151 (2023).
- [3] Y. Wang et al. *Science* 382, 6666 (2023).
- [4] S. Phark et al. *Adv. Sci.* 10, 2302033 (2023).



Tomography Scan of Charge Density Wave in NbSe<sub>2</sub>**Chun-Liang Lin**Department of Electrophysics, National Yang Ming Chiao Tung University, Hsinchu,  
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Charge density wave (CDW) resulting from a periodic distortion in the lattice creates new orders beyond the original lattice. In 2H-NbSe<sub>2</sub>, one of the layered transition metal dichalcogenides (TMD), the 3×3 charge order appears in two-dimensional (2D) layers. Although CDW can be observed by different techniques, the spatial distribution within a 2D layer has never been systematically visualized. Here, by using scanning tunneling microscopy (STM) and density functional theory (DFT), we monitored the evolution of CDW along the c-axis and realized a tomography scan of CDW of the topmost layer. The results show that the appearance of the CDW varies while tuning the tunneling current and undergoes a transition from the outermost Se level to Nb level. The calculation of orbital charge distributions shows that both CDW intensity modulation and the transition are strongly correlated with the distribution of Se 4p orbitals and Nb 4d orbitals.



Reference:

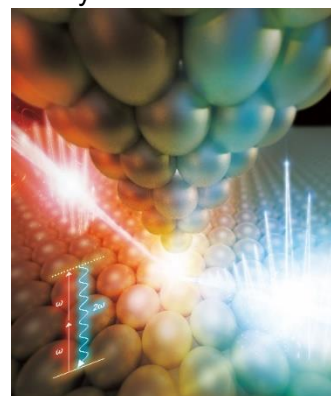
[1] Jyun-Yu Wu, Chun-Liang Lin\* et al. arXiv:2303.12053v1

## Pioneering tip-enhanced nonlinear optics and spectroscopy

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Plasmonic excitation at the nanogap between a metallic nanotip and a surface results in the strong localization and enhancement of the electromagnetic field, thereby amplifying weak spectroscopic signals from sub-diffraction-limited volumes. This mechanism of light compression and amplification, when integrated with scanning probe microscopy, facilitates nanoscale optical mapping of materials. While prior studies in tip-enhanced nanoscopy have largely focused on linear optical responses such as light scattering and photoluminescence, recent years have seen significant advancements in the nanoscale detection of nonlinear optical processes, achieving notable sensitivity and spatial resolution [1-3]. A critical limitation in these studies on tip-enhanced nonlinear optics, however, is the restricted wavelength range, which is typically limited to the visible to near-infrared region. These wavelengths are too short to resonantly excite molecular vibrations, which typically resonate with mid-infrared light, thus preventing the application of tip-enhanced nonlinear optics in molecular vibrational nanoscopy.

In this study, we directly tackle this issue. To exploit the tip-enhanced nonlinear optical phenomena as an advanced molecular spectroscopic technique, we explore the nonlinear optical properties of tip-substrate nanocavities over a broader wavelength range, extending from the visible to the mid-infrared region. We focus on tip-enhanced second-harmonic generation (TESHG) induced by a wavelength-tunable femtosecond laser, demonstrating efficient tip-enhancement of nonlinear optical effects across this extended wavelength range (Fig. 1) [4]. Furthermore, we show that this TESHG response can be significantly modulated and controlled by an external electric field. Leveraging these insights, we recently established nanoscale tip-enhanced molecular spectroscopy by extending our TESHG setup and developing a vibrational nanoscopic system based on tip-enhanced sum-frequency generation (TESFG). By irradiating the tip-substrate nanocavity with both mid- and near-infrared femtosecond pulses, we successfully captured vibrational SFG nanoscopic signals from an ultrathin molecular layer not only on (plasmonic) Au surfaces but also on (non-plasmonic) Pt and Ni surfaces. Our results lay a new foundation for understanding and precisely manipulating nonlinear optical phenomena in plasmonic nanocavities, opening new avenues for detailed exploration of correlated chemical and topographic information through tip-enhanced nonlinear nanoscopy.



**Figure 1 Nonlinear optical effect at a plasmonic nanogap between a tip and a substrate.**

- [1] C.-F. Wang and P. Z. El-Khoury, *J. Phys. Chem. Lett.* **13**, 7350 (2022). [2] C.-F. Wang and P. Z. El-Khoury, *J. Phys. Chem. Lett.* **12**, 10761 (2021). [3] V. Kravtsov *et al.*, *Nat. Nanotechnol.* **11**, 459 (2016). [4] **S. Takahashi** *et al.*, *J. Phys. Chem. Lett.* **14**, 6919 (2023).

## Poster presentation

Please be aware that No. 1 to 32 have been nominated for the Poster Award. We invite all participants to select up to three posters that they found outstanding and to record their choices on the provided ballot. Ballots will be distributed at the conference reception. After poster session, we kindly ask you to deposit your completed ballot in the designated collection box.

1. STM observation of the initial Ag overlayer formation on the Ni(110) surface  
**Aoi Mizuhara**, Tsuneo Fukuda, Kenji Umezawa
2. Using AFM Manipulation of Fluorescence On and Off to Reveal the Partition of Tags between Gel and Fluid Phases  
**Jia-Ru Yu**, He-Chun Chou, Wei-Ssu Liao, Chi Chen
3. Clarifications of local interactions through image processing of the data acquired from energy materials by scanning probe microscopy  
**Sota Tsubokura**, Shoya Kawano, Yumiko Imai, Tadashi Ueda, Kei-ichi Nakamoto, Hirohisa Hioki, Haruo Noma, Taketoshi Minato
4. The Coulomb interaction between single MgNc molecules and insulating thin films on a metal substrate -Controlling molecular optical properties from the substrate-  
**Hiroki Nanbu**, Hiroshi Imada, J. Ahn, M. Lee, X. Ouyang, Atuya Muranaka, J. Jung, H. Lim, Yousoo Kim
5. Analysis of Water Adsorption On TiO<sub>2</sub>(110)-(1x2) Surface By Scanning Tunneling Microscopy  
**Fengxua Li**, Zhuo Diao, Daiki Katsube, Linfeng Hou, Hayato Yamashita, Masayuki Abe
6. Chloride-Gated Electrical Switching of Single-Molecule Junction of Anion Receptor  
**Harunari Okura**, Bui Okada, Hiromitsu Maeda, Tomoaki Nishino
7. Visualization and Characterization of Surface Plasmon Polaritons Propagating at a Buried Metal/Dielectric Interface Sensitized by Photofunctional Quantum Dots  
**Kazuki Kamada**, DaeGwi Kim, Masahiro Shibuta
8. STM study of anomaly CDW formation on layered material NbSe<sub>2</sub>  
**Ryo Ichikawa**, Toyokazu Yamada
9. A Useful Method of Observing Diatom Frustules via Digital Holographic Microscopy  
**Makoto Saito**, Masaki Kitamura, Yuki Ide, Minh Hieu Nguyen, Binh Duong Le, Anh Tuan Mai, Daisuke Miyashiro, Shigeki Mayama, Kazuo Umemura

10. Synthesis and spectroscopic measurements of large-area hydrogen boride sheets  
**Kazuki Yamaguchi**, Masato Niibe, Toshihide Sumi, Xiaoni Zhang, Eiken Nakamura, Kiyohisa Tanaka, Koji Nakanishi, Kazuhiro Kanda, Masafumi Horio, Takahiro Kondoh, Iwao Matsuda
11. In-situ Evaluation of Solid Layer Formation at Superconcentrated Electrolyte/Electrode Interface  
**Akito Kobayashi**, Masanori Nagasaka, Taketoshi Minato, Katsuyoshi Ikeda, and Kenta Motobayashi
12. Atomically demonstration of SnO<sub>2</sub> (4x1) reconstruction by STM/AFM  
**L.Hou**, D.Katsube, T.Ishibe, Y.Nakamura, H.Yamashita, M.Abe
13. Fabrication of plasmonic probes for tip-enhanced Raman spectroscopy using FIB  
**Kazunori Hirose**, Kaifeng Zhang, Masanori Hara and Masamichi Yoshimura
14. Development of a high coherence and ultrafast electron source  
**Yui Iwasaki**, Yuri Saida, Ryota Nishimori, Masaki Hada
15. Mechanism of Binary Conductance Switching of Fullerene Single Molecules in Break Junction Experiments  
**Aoshi Yamane**, Fujii Shintaro, Tomoaki Nishino
16. Development of integrated system for machine-learning automatic RHEED analysis and MBE chamber  
**Toshiro Osawa**, Asako Yoshinari, Masato Kotsugi, Naoka Nagamura
17. Development of automatic Fermi surfaces analysis using data science  
**Daichi Ishikawa**, Kentaro Fuku, Yoshio Miura, Yasuhiko Igarashi, Yuma Iwasaki, Yuya Sakuraba, Koichiro Yaji, Alexandre Lira Foggianto, Arpita Varadwaj, Naoka Nagamura, Masato Kotsugi
18. Analysis of DMI Energy in the Formation Process of Skyrmions Using an Extended Landau Free Energy Model  
**Yotaro Machida**, Michiki Taniwaki, Alexandre Lira Foggianto, Chiharu Mitsumata, Ippei Obayashi, Yasuaki Hiraoka, Kyoko Ishizaka, Masato Kotsugi
19. Selective dehydrogenation of methanol on Cu(977) and Pd/Cu(977) surfaces  
**Yoshiko Sakaguchi**, Wataru Osada, Kozo Mukai, Shunsuke Tanaka, Jun Yoshinobu
20. STM atom manipulation of single Ag atoms on Si(111)-(7×7) at room temperature  
**Junya Okuyama**, Diao Zhuo, Masayuki Abe, Hayato Yamashita
21. Identify the Relationship between Crystal Structure and Electronic State of Boron Nitride Using Density Functional Theory and Machine Learning  
**Reika Hasegawa**, Arpita Varadwaj, Alexandre Lira Foggianto, Masahito Niibe, Yasunobu Ando, Iwao Matsuda, Masato Kotsugi

22. Observation of ZnO(0001) surface structure by scanning tunneling microscopy  
**Yamato Tashiro**, Masayuki Abe , Hayato Yamashita
23. Preparation of a solution containing copper complexes with thiocyanate groups in a hydrophobic solvent and solid-state transformation of the film formed using the solution into copper thiocyanate  
**Kota Kobayashi**, Takeshi Tanaka, Yoichi Nakashima, and Takayo Moriuchi
24. Ultrafast dynamics of Charge-density wave in 1T-TiSe<sub>2</sub>  
**Yu Mizukoshi**, Takumi Fukuda, Muneaki Hase
25. RHEED analysis methods using machine learning and application for film preparation  
**Asako Yoshinari**, Toshiro Osawa, Shingo Takezawa, Shunsuke Sato, Yuma Iwasaki, Yasunobu Ando, Tarojiro Matsumura, Rei Hobara, Shuji Hasegawa, Masato Kotsugi, Naoka Nagamura
26. Investigating energy transfer from Alq<sub>3</sub> molecules to Si by pump-probe spectroscopy  
**Yu-Chan Tai**, Wen-Yen Tzeng, Jhen-Dong Lin, Yi-Hou Kuo, Fu-Xiang Rikudo Chen, Ruei-Jhe Tu, Ming-Yang Huang, Shyh-Shii Pai, Nick Weihang Chang, Sheng-Yang Tseng, Chi Chen, Chun-Liang Lin, Atsushi Yabushita, Shun-Jen Cheng, Chih-Wei Luo
27. Monitoring of the Oxygen Partial Pressure inside the Gas Diffusion Layer of Polymer Electrolyte Fuel Cells during High-Temperature Power Generation  
**Christopher Schreiber**, Junji Inukai
28. Study on Metal-Supported Photocatalyst Materials Using High-Speed Atomic Force Microscopy  
**Ryotaro Tani**, Hayato Yamashita, Masayuki Abe
29. Atomic-Level Patterning of Si(111) Surface using STM Lithography  
**Kensho Tsukuda**, Masayuki Abe, Hayato Yamashita, Jo Onoda, Linfeng Hou
30. Visualization of friction distribution in stearic acid solution at cross-sectional direction using simultaneous system of FM-AFM / LFM  
**Yuya Yamaguchi**, Haruto Gato, Akinori Kogure, Hiroshi Arai, Masahiro Ota, Kaisei Sato, Shinya Sasaki
31. Study of hydrogen addition and desorption processes in iridium complex using transmission FT-IR  
**Tianle Wang**, Wataru Osada, Kozo Mukai, Shunsuke Tanaka, Takanori Koitaya, Kenichi Fujita, Jun Yoshinobu
32. Study on a method to grow self-assembled-monolayer covered tips for quantitative Atomic Force Microscopy  
**Koji Tomofuji**, Toshikazu Kitagawa, Naruo Sasaki, Dai Kobayashi, Hideki Kawakatsu
33. TPD Study of Argon Hydride ArH from Argon Implanted Pd(111) Surfaces  
Hayato Naka, Aruku Fukushima, Kohei Izawa, Tomotaka Hirano, **Kazuo Watanabe**

34. Selective coupling of coherent optical phonons in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  with electronic transitions  
**Kunie Ishioka**, Alexej Pashkin, Christian Bernhard, Hrvoje Petek, Xin Yao, and Jure Demsar
35. Construction of optics combined low temperature STM  
**Alexina Ollier**, Pegah Farahi Shandiz, Jiyeon Lee, Alexina Ollier, Lei Fang, Minsu Seo, Soohyeong Lee, Sangwon Yoon, Andreas J. Heinrich and Wonjun Jang
36. Visualization of Band Shifting and Interlayer Coupling in  $\text{W}_x\text{Mo}_{1-x}\text{S}_2$  Alloys Using Near-Field Broadband Absorption Microscopy  
**Po-Wen Tang**, Shiue-Yuan Shiau, He-Chun Chou, Xin-Quan Zhang, Jia-Ru Yu, Chun-Te Sung, Yi-Hsien Lee, and Chi Chen
37. Nanoscopic Observation and Control of Chiro-Optical Force  
**Junsuke Yamanishi**, Hyo-Yong Ahn, and Hiromi Okamoto
38. Investigation of 3D-Fermi-surface by using the the angle-resolved photoelectron spectroscopy with the synchrotron radiation  
**Shin-ichiro Tanaka**, Shigemasa Suga, Keiji Ueno, Keisuke Fukutani, Seiji Makita, Fumihiko Matsui, Kiyohisa Tanaka
39. Tip-enhanced Raman study of pentacene derivative on Ag surface: adsorption structure and dynamics  
**Norihiro Aiga**, Takenori Nagasawa and Satoshi Takeuchi
40. Time-resolved photoemission study of photo-excited carrier dynamics in zinc phthalocyanine thin films grown on HOPG substrate  
**Isamu Yamamoto**, Azuma Junpei, Masaki Imamura, Kazutoshi Takahashi
41. Development of Electronics for Low-temperature Scanning Near-Field Optical Microscopy  
**Tomonori Toyoda**, Takashi Kumagai, Msasyuki Abe
42. Atomic-scale investigation for electronic properties of multiple resonance thermally activated delayed fluorescence molecule  
**Jaehyun Bae**, Miyabi Imai-Imada, Lee Minhui, Hyungsuk Kim, Hiroshi Imada, Youichi Tsuchiya, Takuji Hatakeyama, Chihaya Adachi, Yousoo Kim
43. s-SNOM using kHz laser sources  
**Samuel Palato**
44. Single molecule photonics for nanospectroscopy and beyond  
**Hiroshi Imada**, Miyabi Imai-Imada, Yousoo Kim
45. In-situ Evaluation of Solid Layer Formation at Superconcentrated Electrolyte/Electrode Interface  
**Akito Kobayashi**, Masanori Nagasaka, Taketoshi Minato, Katsuyoshi Ikeda, and Kenta Motobayashi

46. Quantum dynamics of a photoexcited electronic system coupled to an anharmonic oscillator environment  
**Kuniyuki Miwa**, Souichi Sakamoto, and Akihito Ishizaki
47. DNA Investigation by AFM and nano-FTIR  
**Chawewan Sapcharoenkun**, Jun Nishida, Akihiro Otomo, Taketoshi Minato, Ryota Iino, and Takashi Kumagai
48. Electrochemical Imaging of Hydrogen Evolution Reaction at Surface of MoS<sub>2</sub> Nanoribbons by Scanning Electrochemical Cell Microscopy  
**Kaito Hirata**, Kota Honda, Ma Zongpeng, Pablo Solís Fernández, Hiroki Ago, Yasufumi Takahashi
49. Metastability in the Insulator-Metal Transition for Individual VO<sub>2</sub> Nanoparticles  
K. Nishikawa, J. Nishida, T. Kumagai, **Y. Watanabe**
50. Nano-scale study of reaction film using zinc dialkyl dithiophosphates induced by shear stress  
**Kaisei Sato**, Shinya Sasaki
51. Multimodal photoemission investigation of 1T-TaS<sub>2</sub> chiral charge density wave phase transition by soft X-ray/VUV photoelectron momentum microscope  
**Fumihiko Matsui**, Kenta Hagiwara, Shigemasa Suga
52. Reaction Mechanisms at the Interfaces between Halogen Ions and Metal Electrodes in Liquid Electrolytes Analyzed by Scanning Probe Microscopy  
Yumiko Imai, Tadashi Ueda, Kei-ichi Nakamoto, **Taketoshi Minato**

## Luncheon Seminar

### *Quantum Design Japan*



*Introduction of neaSCOPE that realize wavelength-independent nanoscale optical imaging & spectroscopy across THz, IR and visible spectral ranges by combining SPM with optics*

The neaSCOPE was originally developed as a scattering-type scanning nea-field optical microscope (s-SNOM). Owing to unique patented detection, neaSCOPE realize wavelength-independent 10-20nm optical resolution imaging and spectroscopy across THz, IR and visible spectral ranges without background. We can offer integrated system with light sources that guarantee reliable data. Furthermore, it can be combined with your own light source such as synchrotron beam line. Over 10 neaSCOPEs has been installed at synchrotron facilities around the world. These days, neaSCOPE is developed to support various measurement modes both optical and mechanical for comprehensive and correlative nanoscale analytics.

I'm going to introduce principal of measurement, instrumentation and the latest applications.

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*TBA*