1st IMS-FHI Symposium: “Emerging Techniques of Scanning Probe Microscopy”

Online, July 12th–13th, 2021

Institute for Molecular Science (Japan) & Fritz-Haber Institute (Germany)

Scanning probe microscopy (SPM) has developed as a core method in nanoscale science and technology. Its applications now spread over a broad range of research fields including physics, chemistry, biology and medical sciences. The advancement of SPM technologies has also cultivated interdisciplinary areas and will further expand the possibility. In this joint symposium between Institute for Molecular Science, Japan (IMS) and Fritz Haber Institute, Germany (FHI), we discuss the latest development and perspective of SPM technologies including low temperature experiments, near-field optical microscopy under ambient condition and in solution, electrochemical and biomolecular investigations.

Takashi Kumagai, Center for Mesoscopic Sciences, Institute for Molecular Science, Japan

Program

12.7.2021 (Day 1)

15:55 (Japan), 8:55 (Germany):
Takashi Kumagai
“Opening remarks”

16:00-16:40 (Japan), 9:00-9:40 (Germany):
Borja Cirera (Fritz Haber Institute)
“Design and characterization of organic nanomaterials combining SPM and TERS”

16:40-17:20 (Japan), 9:40-10:20 (Germany):
Taketoshi Minato (Institute for Molecular Science)
“Electrode/Electrolyte Interface Analyzed by Scanning Probe Microscopy”

17:20-18:00 (Japan), 10:20-11:00 (Germany):
Tomoko Shimizu (Keio University, Japan)
“How to bridge the "materials gap" in high resolution AFM/STM?”

18:00-18:30 (Japan), 11:00-11:30 (Germany):
Leonard Gura (Fritz Haber Institute)
“High Speed STM: Implementation and Application of Spiral Scan Geometries”

13.7.2021 (Day 2)

16:00-16:40 (Japan), 9:00-9:40 (Germany):
Akitoshi Shiotari (FHI)
“Control of single-molecule reactions by high spatial resolution AFM”

16:40-17:20 (Japan), 9:40-10:20 (Germany):
Chi Chen (Research Center for Applied Sciences, Academia Sinica, Taiwan)
“Near-field optics: from the viewpoint of scanning probe microscopy”

17:20-18:00 (Japan), 10:20-11:00 (Germany):
Jun Nishida (Institute for Molecular Science)
“Ultrafast nano-imaging of polaron dynamics and coupling in a lead halide perovskite”

Design and Charaterization of Organic Nanomaterials Combining SPM and TERS

Borja Cirera, Postdoctoral Researcher
Department of Physical Chemistry, Fritz Haber Institute

In the last decades, a deeper understanding of on-surface reactions and the discovery of new mechanisms prohibited in solution resulted in the fabrication with atomic precision of myriad novel organic materials, frequently investigated with scanning probe microscopy (SPM). However, SPM lacks in general the required chemical sensitivity to properly investigate the local physico-chemical properties of the products. Just recently, Tip Enhanced Raman Spectroscopy (TERS) in plasmonic nanocavities has reached sub-nanometer resolution, visualizing chemical heterogeneities and vibrations of adsorbates in the real space [1,2]. The required Raman sensitivity relies on different enhancement mechanisms present in the SPM junction, whose relative importance is still under debate. Here, I will show our latest results of a single C_{60} between a silver tip and various metallic substrates. The experiment serves as a model system to discuss the diverse factors present in a single molecule junction, finding a novel current-driven enhancement upon molecular point contact (MPC) formation. The resulting exceptionally high sensitivity, operative even for the weak plasmonic Pt(111) substrate, can be exploited to further understand and control chemical reactions at the atomic scale on a large diversity of surfaces. Furthermore, the giant enhancement makes accessible the observation of subtle anti-Stokes Raman signals, enabling the investigation of light-matter interactions in non-equilibrium quantum transport systems.

[1] J. Xu et al., *Science* **371**, 818 (2021).
[2] J. Lee et al., *Nature* **568**, 78 (2022).

Short Biography:
Dr. Cirera obtained his doctoral degree in physics in January 2018, under the supervision of . Prof. Rodolfo Miranda and Prof. David Ecija at IMDEA Nanoscience, Spain, under the title “On-surface Design of Lanthanide-based Nanoarchitectures”. In January 2019, he joined as a postdoctoral researcher in the Nanoscale Surface Chemistry group of Dr. Takashi Kumagai of the Fritz Haber Institute, Germany.

Electrode/Electrolyte Interface Analyzed by Scanning Probe Microscopy

Taketoshi Minato, Senior Reasercher
Institute for Molecular Science, National Institutes of Natural Sciences

By understanding the physical properties and reaction mechanisms at the interface between electrode and electrolyte, the developments of the energy conversion system would be expanded. In this presentation, our recent achievements of the investigation of the interface for energy conversion system by scanning probe microscopy are shown. The enchancements of the electron conductivity by ordering of the lithium ions in electrode, the direct observation of the electric double layer, the viscosity mapping at the interface will be shown. In addition to these, the reaction mechanism at the interface in working rechargeable batteries will be shown.

Short Biography:

Dr. Minato received his Ph. D degree in science from Tokyo Institute of Technology in 2005. He studied the electronic structure of titanium dioxide and its interaction with gold nano-clusters. After receiving Ph. D, he became a special postdoctoral researcher, surface chemistry laboratory, RIKEN. He extended his works on the electronic structure of metal oxides. At 2007, he moved to Tohoku university as an assistant professor. He applied his knowledge of fundamental theories and experimental techniques to complex system of electrode/electrolyte interface. He joined surface & interface science laboratory, RIKEN as a ASI research scientist and became an associate professor, office of society-academia collaboration for Innovation, Kyoto University. He investigated the analysis and application of electrode/electrolyte interface in rechargeable batteries. From 2020, he is extending his works in energy conversion systems as a senior researcher, institute for molecular science, national institutes of natural sciences. He has received several awards for scientists, including Young Scientist Award of the Physical Society of Japan in 2017 (Japan), Young Scientist Award of Green Sustanable Chemistry Awards in 2017 (Japan), The Special Prize for The High Technology Award for Originality in 2019 (Japan), and the Docomo Mobile Science Award in 2019 (Japan).

How to bridge the "materials gap" in high resolution AFM/STM?

Tomoko K. Shimizu, Associate Professor
Department of Applied Physics and Physico-Informatics, Keio University

Materials gap is the term describing the difference between materials used in industry and those studied experimentally in laboratories. Scanning tunneling microscopy (STM) and atomic force microscopy (AFM) with atomic and submolecular scale require samples that are atomically flat and homogeneous all over the surface. It is, however, that real catalysts, gas adsorbents and filters used in industry are mostly in the form of nanoparticles, porous materials, or thin films of these. In order to investigate these technologically relevant nanomaterilas at the atomic scale, we propose a way to image 3D objects using so-called multi-pass method. We are also working on the development of a new microscope that is capable of scanning from micrometer to nanometer scale simultaneously. Methods to prepare samples suitable for STM/AFM measurements will also be discussed based on our recent trials using oxide nano particles dispersed in organic solvent, and porous organic thin films fabricated at the air-liquid interface.

Short Biography:

Dr. Shimuzu received her PhD degree from University of California, Berkeley, USA, in May 2007, with theme “Water adsorption on Ru(0001) studied by low-temperature ultra-high vacuum scanning tunneling microscopy”. In July 2007, she joined RIKEN and worked for Prof. Maki Kawai and Dr. Yousoo Kim. She also worked as a senior researcher at Nanomechanics group in the National Institute for Materials Science (NIMS) between 2014 and 2018. In April 2018, she was appointed Associate Professor in the department of Applied Physics and Physico-Informatics, Faculty of Science and Technology, Keio University. She has received MEXT Young Researcher Award in 2018.

High Speed STM:

Implementation and Application of Spiral Scan Geometries

Leonard Gura, PhD-Candidate
Department of Chemical Physics, Fritz Haber Institute

Scanning Probe Microscopy (SPM) provides powerful tools for surface science applications. Atomic Force Microscopy (AFM) and Scanning Tunneling Microscopy (STM) stand out due to their very high spatial resolution. However, until now its low time resolution impedes real time observations of dynamic processes. One major factor that limits the frame rate is the scan geometry. The conventional line-by-line scan geometry consists of sharp triangular input signals that introduce electronic and mechanical noise to the system. Low signal to noise ratios and severe image distortions are the result. To overcome this limitation, scan geometries with smooth input signals must be used. While in AFM alternative scan geometries have already been applied, in STM the scan pattern is barely altered from the conventional raster geometry. Here, I will present the first high-speed STM data acquired with an unconventional scan pattern. The used pattern consists of smoothly connected spiral geometries. The implementation of the signal is generally applicable and serves as a starting point for future developments to increase the frame rate in STM. First measurements on the O(2x2) superstructure on Ru(0001) allowed to resolve the occupation of the intermediate state along the diffusion path of a jumping oxygen atom. In future, the presented approach to high-speed STM will be applied to resolve structural changes in oxide thin film systems at elevated temperatures.

Short Biography:

Leonard Gura obtained his Master of Science degree in materials science in 2017 at the Technical University of Darmstadt, Germany. Since then, he is working in the group of Prof. Freund at the Fritz Haber Institute, Germany. The scope of his work is to increase the frame rate in STM measurements to resolve dynamics at the atomic scale.

Control of single-molecule reactions by high spatial resolution AFM

Akitoshi Shiotari, Research group leader
Department of Physical Chemistry, Fritz Haber Institute

Noncontact atomic force microscopy (ncAFM) is a powerful method to visualize surface topographies by detecting forces between the tip-apex and surface atoms. By using an atom/molecule-functionalized tip, the spatial resolution of ncAFM images can be enhanced drastically [1,2]. In addition to such direct observation with atomic resolution, ncAFM has a considerable potential to control chemical reactions of individual molecules by stimulation from the probe tip that can be moved with sub-angstrom precision.

I will report the dehydrogenation of aromatic hydrocarbons catalyzed by a ncAFM tip [3]. Although the intramolecular cyclodehydrogenation of organic molecules is essential for on-surface synthesis to yield nanographene materials, its elementary steps have not been clarified thoroughly. In this study, we utilized a metal tip of low-temperature ncAFM as a manipulable metal surface. The proximity of the tip locally induced the covalent C–H bond dissociation, indicating the importance of contacting a metal surface to hydrogen atoms of hydrocarbon during the reaction step to yield nanographene.

[1] L. Gross et al., Science **325**, 1110 (2009).
[2] A. Shiotari et al., Nat. Commun. **8**, 16089 (2017).
[3] A. Shiotari et al., Nano Lett. **20**, 8339 (2020).

Short Biography:

Dr. Shiotari obtained his doctoral degree in chemistry in March 2015, under the guidance of Assoc. Prof. Hiroshi Okuyama at Kyoto University, Japan, with theme “Reactivity of Nitric Oxide on Copper Surfaces Elucidated by Direct Observation of Valence Orbitals.” In April 2015, he worked with Assoc. Prof. Yoshiaki Sugimoto at the University of Tokyo, Japan, as an assistant professor. In May 2021, he moved to Fritz Haber Institute, Germany, as a group leader. His interests include atomic-scale surface science and single-molecule measurements using scanning probe microscopy. He won the Young Scientist Presentation Award of the The Japan Society of Applied Physics in 2016 and the Young Scientist Award of the Physical Society of Japan in 2021.

Near-field optics: from the viewpoint of scanning probe microscopy

Chi Chen, Assistant Research Fellow
Research Center for Applied Sciences, Academia Sinica, Taiwan

Scanning near-field optical microscopy (SNOM or NSOM) is a branch of optical imaging techniques, which combines optics with scanning probe microscopy (SPM) to achieve sub-diffraction-limit optical resolution. Various ways of combing a STM or an AFM with optical access will be introduced in the talk, including STM-electroluminescence (STM-EL), STM-based tip-enhanced Raman (STM-TERS), and AFM based aperture SNOM (*a*-SNOM).

Based on our recent efforts in developing a-SNOM in glove box and water, *a*-SNOM results of 2D materials and lipid bilayers will be presented here. For 2D lateral heterostructures, we resolved a PL depletion at the boundary between MoS_2 and WS_2 due to the intermix of Mo and W atoms. In the case of lipid bilayers, we visualized the transition from the liquid-ordered (*Lo*) to the liquid-disordered (*Ld*) phase by temperature-controlled SNOM operating in water. In addition to experimental results, we will briefly summarize the problems, artifacts, and challenges in near-field optics at the end of the talk.

Short Biography:

Dr. Chi Chen obtained Ph.D. in 2009 under the supervision of Prof. Wilson Ho at the University of California-Irvine, focusing on STM-EL of single molecules. She then joined the research group guided by Prof. Satoshi Kawata at RIKEN, Japan, as a postdoctoral associate. Her work of imaging of carbon nanotubes by TERS has been selected as “100 Achievements at RIKEN in 100 years.“ Since 2013, she joined Academia Sinica in Taiwan as an assistant research fellow. Her research interests include near-field optical spectroscopy and microscopy (SNOM), Tip-enhanced Raman spectroscopy (TERS), AFM/STM/SNOM instrumentation, and their applications to study various nanomaterials.

Ultrafast nano-imaging of polaron dynamics and coupling in a lead halide perovskite

Jun Nishida, Assistant Professor
Center for Mesoscopic Sciences, Institute for Molecular Science

Lead halide perovskites have attracted intense interets as defect-tolerant, flexible, and economical optoelectronic materials. Their extraordinary photovoltaic performance is believed to be associated with “large polaron” formation, where the soft perovskite lattitce deforms across multiple unit cells to stabilize the photoinduced carriers. On the other hand, the spin-coated films of perovskites are known to be highly heterogeneous in their optoelectronic response, at multiple length scales from microscopic lattice to mascrsopic device scales. However, the relationship between such optoelectronic heterogeneity and the underlying electron-phonon interactions has remained elusive. Here, we address such fundamental polaronic heterogeneity using infrared scattering scanning near-field optical micorscopy (IR *s*-SNOM) and ultrafast IR *s*-SNOM, by taking advantage of their access to low-energy responses at the nanoscale. While infrared vibrational nano-spectroscopy reveals the spatially disordered coupling between an organic cation and a perovskite lattice, ultrafast infrared nano-imaging of polaron absorption directly tracks the spatio-temporal dynamics of photoinduced polaron within a spin-coated film. The unraveled spatial disorder in the dynamic lattice elasticity and polaron dynamics is critical for understanding and controlling carrier dynamics in perovskite-based devices.

Short Biography:

Dr. Nishida received his PhD degree from Stanford University, USA, in January 2018, with his thesis titled “Development of nonlinear infrared spectrosopic methods to probe molecular dynamics in funational materials”. During his PhD, he received Stanford Graduate Fellowship (SGF) from 2014 to 2016. In December 2017, he joined University of Colorado Boulder with a research fellowship awarded from Japan Society for the Promotion of Science and collaborated with Dr. Markus B. Raschke. In April 2021, he was appointed to an assistant professor at Center for Mesoscpic Sciences in Instutite for Molecular Science, Japan.