CEMS Topical Meeting Online

Advanced Visualization of Electrons, Atoms, and Molecules

October 29, 2020 (Thu)

Progress in technologies of measurement and analysis is notable because it enables to enlarge the limitations such as sensitivity, spatial resolution, and data accumulation time. Hardware like probing or detection system has been amazingly improving for a couple of decades. Furthermore, development in data processing software based on application of statistical and information technologies has been drastically rising nowadays. This topical meeting is focusing on state-of-the-art technologies in the field of measurement and analysis feasible to characterize emergent matter phenomena by visualization of electrons, atoms, and molecules.

13:00–13:10 **Opening**

13:10–14:00 (*Long talk)

Shigeki Kawai

(NIMS)

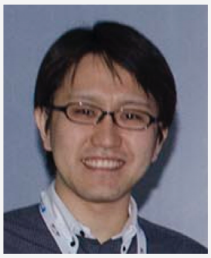
"On-surface chemistry studied with high-resolution scanning probe microscopy"

14:00–14:35

Manabu Hoshino

(RIKEN CEMS)

"Evaluation of 'to-be-collected' diffraction data using information technology"



14:35–15:10

Kenichi Kato

(RIKEN RSC)

"Data-driven total scattering measurements by synchrotron X-rays —Aiming at visualization of heterogeneous phenomena—"

15:10–15:30 **Break**

15:30–16:05

Ryo Ishikawa

(The Univ. of Tokyo)

"Advanced electron microscopy for point defects"

16:05–16:40

Keiki Fukumoto

(KEK)

"Electron dynamics in organic heterostructures"

16:40–17:30 (*Long talk)

Ken Onda

(Kyushu Univ.)

"Structural dynamics in photofunctional materials studied by time-resolved infrared spectroscopy"

17:30–17:40 **Closing**

https://cems.riken.jp/topicalmeeting/004_visualization/

RIKEN CEMS

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On-surface Chemistry Studied with High-Resolution Scanning Probe Microscopy

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Recent advances in state-of-the-art probe microscopy with a functionalized tip allow us to observe inner structures of molecules on surfaces [1]. This high-resolution imaging technique is beneficial to investigate single and self-assembled molecules, as well as products of on-surface reaction. Furthermore, combining with the Ullmann-type reaction and/or tip-induced manipulation of atom and molecule, syntheses of various nanocarbon materials became possible [2].

In this talk, I will present our recent results on on-surface chemistry studied with high-resolution atomic force microscopy/scanning tunneling microscopy under ultra-high vacuum at low temperature. Various bromo-substituted molecules were deposited on metal surfaces, and subsequently annealed at 100~400 ºC. Since C-Br bonds are cleaved in the process, molecules are conjugated with each other. With appropriate precursor molecules, novel compounds [3] and functionalized nanocarbon materials, such as boron-doped [4] and boron-nitrogen-doped [5] as well as three-dimensional graphene nanoribbons (GNR), have been synthesized. We found that these GNRs offer attractive experiments such as friction [6] and local probe chemical reaction [7].

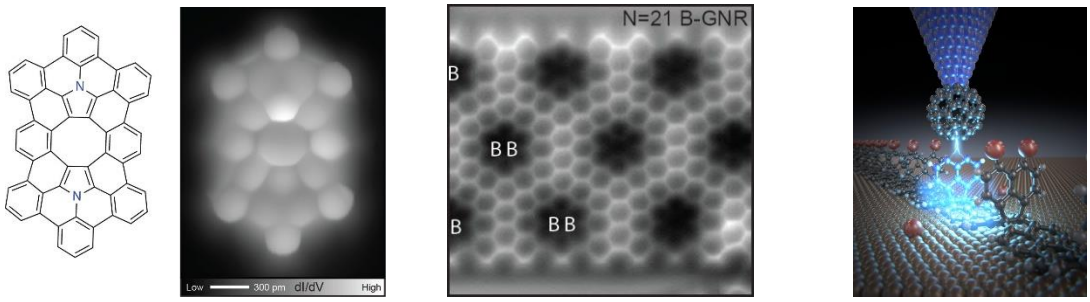

Fig.1: On-surface syntheses of a π-extended diaza[8] circulene (left)[3], boron-doped GNR (center)[4], and three-dimensional GNR (right)[7].

[1] L. Gross *et al*., Science **325**, 1110 (2009).
[2] J. Cai *et al*., Nature **466**, 470 (2010)
[3] K. Nakamura *et al*., J. Am Chem. Soc. **142**, 11363 (2020)
[4] S. Kawai *et al*. Nat. Commun. **6**, 8098 (2015)
[5] S. Kawai *et al*., Sci. Adv. **4**, eaar7181 (2018).
[6] S. Kawai *et al*., Science **351**, 957 (2016).
[7] S. Kawai *et al*., Sci. Adv. **6**, eaay8913 (2020).

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CEMS Topical Meeting Online

Evaluation of '*to-be-collected*' diffraction data using information technology

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Crystal structure analysis essentially provides three-dimensional distribution of electron density in a crystal specimen. Using that distribution, molecular and crystal structure are constructed, refined, and evaluated. Due to this principle of crystal structure analysis, researcher who will perform crystal structure analysis carefully design a strategy of diffraction data collection for visualizing realistic and informative electron density distribution. In this talk, our developed methodology[1], which is useful to the strategy building via evaluation of to-be-collected diffraction data generated by information technology, is introduced with showing a practical example.

Generation of to-be-collected diffraction data is based on stochastic sampling from a probability distribution using a computer. In our methodology, the parameter inherent in a probability distribution of diffraction data peculiar to a subject crystal is precisely estimated from a preliminary-collected small diffraction data set by Bayes' theorem, which is a theory basically used in information technologies. The generated data set is used for optimizing X-ray exposure time to collect quantitative diffraction intensities. Crystal structure analysis using diffraction data collected along the strategy with the optimized X-ray exposure time clearly visualized electron density distributions of equivalent three lone-pairs around an oxygen atom in a sulfonyl group (Figure).

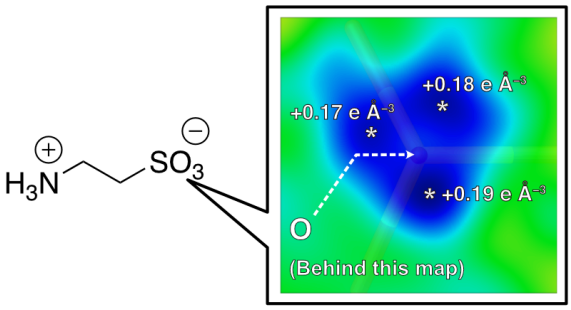

Figure. Electron density distribution around a selected oxygen atom in taurine ((2-aminoethane-1-sulfonic acid, $C_2H_7NO_3S$). Positive peak positions are marked by '*' with the corresponding amplitude. The color scheme and the density limit [blue: positive (max.: 0.18 e $Å^{-3}$); green: zero].

[1] M. Hoshino, Y. Nakanishi-Ohno, D. Hashizume, *Sci. Rep.*, **2019**, *9:11886* doi:10.1038/s41598-019-48362-3.

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CEMS Topical Meeting Online

Data-driven total scattering measurements by synchrotron X-rays —Aiming at visualization of heterogeneous phenomena—

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Synchrotron radiation (SR), which is recognized as one of the most powerful analytical tools for materials and life sciences, allows us to visualize physical and chemical phenomena. Taking the advantages of SR, such as high brilliance, adjustable energy and polarization, coherence, and pulsed beams, gives us crystal and electronic structures on a wide scale in space and time. From SR X-ray diffraction data, crystal structure including electron density can be obtained [1]. In most cases, however, the applications are limited to a perfectly periodic system. Total scattering, which means both Bragg and diffuse scattering, is applicable regardless of structural periodicity [2]. Diffuse scattering is extremely broad and weak compared with Bragg scattering, and therefore total scattering is technically demanding. We developed a total scattering measurement system "OHGI" at the RIKEN Materials Science beamline BL44B2 of SPring-8 to cover a wide range of scattering vector Q with high Q resolution (Fig. 1) [3]. Furthermore, we have recently developed a data-driven correction approach "ReLiEf" to achieve high signal-to-noise ratio (Fig. 2) [4]. A data-driven analysis approach to atomic pair distribution functions is under development to visualize heterogeneous structure inside nanocrystals on a sub-angstrom scale. In this presentation, I will talk about recent advances in terms of both hardware and software.

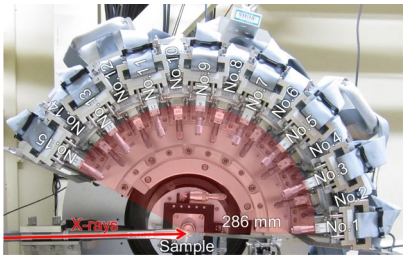

Fig. 1 Hardware development

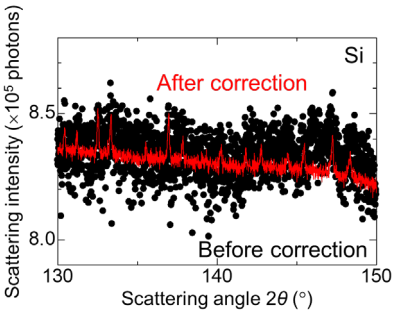

Fig. 2 Software development

[1] K. Kato and H. Tanaka, *Advances in Physics: X* **1**, 55-80 (2016).
[2] T. Egami and S. J. L. Billinge, *Underneath the Bragg Peaks, Structural Analysis of Complex Materials (2nd Edition)*, Pergamon (2012).
[3] K. Kato, Y. Tanaka, M. Yamauchi, K. Ohara, and T. Hatsui, *J. Synchrotron Rad.* **26**, 762-773 (2019).
[4] K. Kato and K. Shigeta, *J. Synchrotron Rad.* **27**, 1172-1179 (2020).

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CEMS Topical Meeting Online

Advanced electron microscopy for point defects

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Materials properties in solids are usually dominated by atomistic structure defects such as vacancy and impurity, and it is therefore important to characterize not only the local atomic configuration but also their chemical bonding state. In recent remarkable progress on differential phase-contrast (DPC) electron microscopy [1,2], it becomes possible to directly visualize electric field and charge density by using atomic-resolution scanning transmission electron microscopy (STEM) combined with segmented or pixelated types of detectors. In this study, we demonstrate that the direct observation of anisotropic electric fields of single Si dopants in monolayer graphene by DPC STEM imaging [3]. The distribution of electric fields of single Si dopants have three or four-fold symmetry rather than circular symmetry, which reflects the surrounding atomic configuration. We also discuss the observed atomic electric fields of Stone-Wales defects and nanopores in bilayer graphene.

In addition to the electric field imaging, it is also important to elucidate the dynamics of single dopants in solids. In STEM, we use relatively high energy electron beam such as 200-keV, and the electron beam has a potential to excite local atomistic diffusion without heating the specimen. We here acquire multi-frames of atomic-resolution annular dark-field (ADF) STEM image with a fast scanning, and we successfully track the single Ce dopants embedded within cubic boron nitride [4]. To push the boundary of atomic-resolution STEM imaging into much faster dynamic observations, we also discuss the recent development of fast scanning coil and fast electron detection system [5].

[1] N. Shibata et al, Nat. Phys. **8,** 611 (2012).
[2] N. Shibata et al, Nat. Commun. **8**, 15631 (2017).
[3] R. Ishikawa et al, Nat. Commun. **9**, 3878 (2018).
[4] R. Ishikawa et al, Phys. Rev. Lett. **113**, 155501 (2014).
[5] R. Ishikawa et al, Microscopy **69**, 240 (2020).

Electron dynamics in organic heterostructures

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We have developed a time-resolved photoemission electron microscopy to visualize electron motion in semiconductors [1-2]. A temporal resolution of 100 fs and a spatial resolution of 100 nm can be achieved simultaneously by using a pump-probe method with femtosecond laser pulses and a PEEM as a detector. In addition, it has an energy resolution of 30 meV by making the wavelength of the light source variable in the UV region [3,4]. Figure 1 show a schematic diagram of the TR-PEEM system.

In this talk we introduce the TR-PEEM method and present our recent work on the electron transfer of a well-defined single-crystalline organic P-N interface (an epitaxial C_{60} layer on single-crystalline pentacene(Pen-SC) as show in Figure 2 (left)). The electron transfer from Pen-SC to C_{60} was directly detected by monitoring the electron density in the LUMO of C_{60} (red plots in Figure 2 (right)) [5].

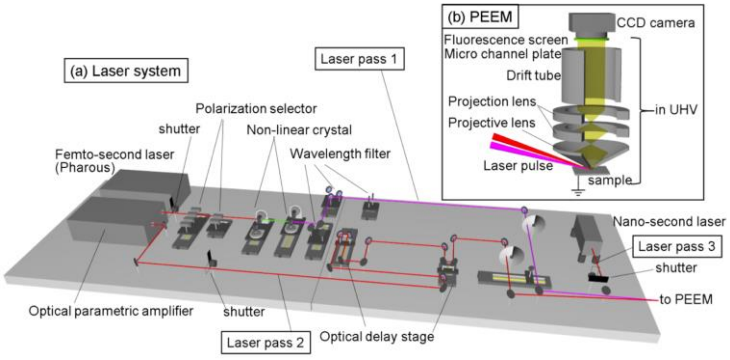

Figure 1: Schematic view of the TR-PEEM system.

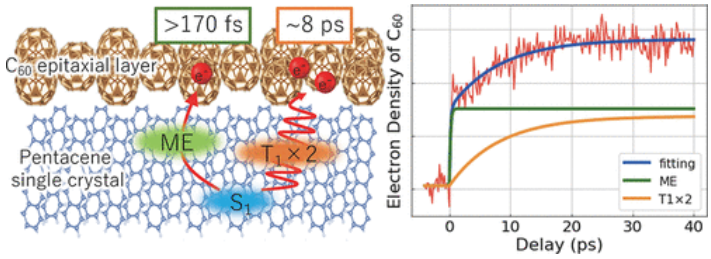

Figure 2: Results of TR-PEEM experiments on a C_{60}/Pen-SC organic heterostructure.

[1] Fukumoto et al., Appl. Phys. Lett., (2014).

[2] Fukumoto et al., Rev. Sci. Instrum., (2014).

[3] Koshihara and Fukumoto, International Pub. Num.: WO2018/159272.

[4] Fukumoto et al., J. Phys. D: Appl. Phys. 53, 405106 (2020).

[5] Iwasawa and Fukumoto et al., J. Phys. Chem. C 124, 13572 (2020).

Structural Dynamics in Photofunctional Materials Studied by Time-resolved Infrared Spectroscopy

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Recently a variety of photofunctional materials have been intensively developed for solving energy and environment problems or for living a better life; however, there are a few in-situ and realtime observation methods for analyzing dynamical processes in these materials though the quick processes upon photoexcitation play key roles for their photofunctions. For now, mostly time-resolved photo-luminescent spectroscopy (TR-PL) and sometime time-resolved ultraviolet-visible transient absorption spectroscopy (TR-UV/VIS) are utilized. Time-resolved infrared vibrational spectroscopy (TR-IR) is potentially powerful tools for analyzing such functional materials because complicated IR spectra particularly in the finger print region contain rich information on not only electronic states but also molecular structures, nevertheless applications of TR-IR to photofunctional materials are limited. Therefore, we developed TR-IR systems for exploring dynamics and unveiled many important phenomena or mechanism in a variety of functional materials (Fig.1): molecular crystals showing photoinduced phase transition [1,2], metal complexes for photocatalysts or artificial photosynthesis [3-6], photo-active liquid crystals [7], graphene oxide [8], and emissive materials for organic light emitting diodes (OLED) [9].

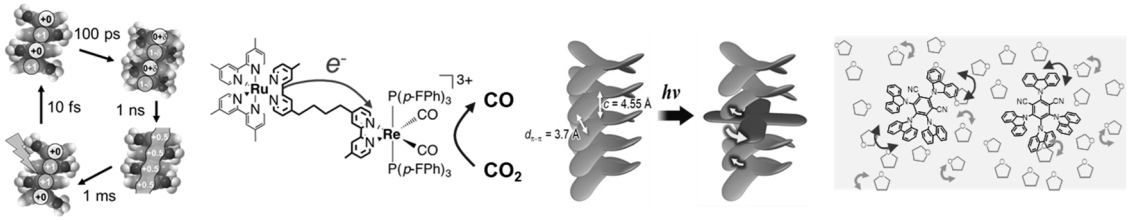

Figure 1. Examples of photofunctional materials studied by time-resolved infrared spectroscopy

[1] N. Fukazawa, M. Shimizu, T. Ishikawa, et al. *J. Phys. Chem. C*, 116, 5892 (2012).
[2] N. Fukazawa, T. Tanaka, T. Ishikawa, et al. *J. Phys. Chem. C*, 117, 13187 (2013).
[3] T. Mukuta, N. Fukazawa, K. Murata, et al. *Inorg. Chem.* 53, 2481 (2014).
[4] T. Mukuta, S. Tanaka, A. Inagaki, et al. *ChemistrySelect* 1, 2802 (2016).
[5] T. Mukuta, P. V. Simpson, J. G. Vaughan, et al. *Inorg. Chem*. 56, 3404 (2017).
[6] Y. Yamazaki, K. Ohkubo, D. Saito, et al. *Inorg. Chem.* 58, 11480 (2019).
[7] M. Hada, S. Saito, S. Tanaka et al. *J. Am. Chem. Soc*. 2017, 139, 15792.
[8] M. Hada, K. Miyata, S. Ohmura, et al. *ACS Nano*, 13, 10103 (2019).
[9] M. Saigo, K. Miyata, S. Tanaka, et al. *J. Phys. Chem. Lett.* 10, 2475 (2019).