

ANNUAL REPORT

2019

**Institute of Advanced Energy
Kyoto University**

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Japan

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FOREWORD



Solar energy, regarded as the origin of life, is produced by nuclear fusion in the extreme conditions at the core of the Sun, and reaches the Earth as light energy, which nurtured terrestrial life over a billion years. In the vast space-time scale of the universe, energy has created the biosphere harmonized with the rich planetary environment, changing the form and shape through nature's ingenious mechanisms. With the various energy-related problems emerging in the current 21st century, a new approach of energy science is desired, which explores next generation energy based on the broader perspectives encompassing the entire coordination of nature.

The Institute of Advanced Energy was established in May 1996 for the purpose of exploring the next-generation energy by probing into the laws and basic principles of nature, and of developing the state-of-the-art technologies to utilize them for practical applications. For this purpose, 14 sections of research areas are organized as three divisions, each dedicated to one of the three basic kinds of energy processes: generation, conversion, and utilization of energy. On top of this, we set up the Laboratory for Complex Energy Processes which also includes 3 sections of research areas. This laboratory organically integrates all the disciplines to enable us to tackle complex energy related issues. Furthermore, we actively promote the internationalization of research and return the fruits of our research back into society incorporating with industry-academia-government collaboration. The institute is also in charge of the Graduate School of Energy Science's Cooperating Chair, which conducts student education and trains researchers in a leading-edge research environment.

The Institute of Advanced Energy focuses on two core research areas: "Plasma and Quantum Energy Science" and "Soft Energy Science". The first topic deals with the generation of energy by nuclear fusion on Earth, which is equivalent to that created in the Sun. The second topic addresses the development of methods for highly efficient energy based on the principles of biology and materials science, which has created the biosphere in the Earth's environment. The form and shape of these two energy sources seem different. However, for instance, plasma, in which nuclear fusion takes place, has been found to be a highly autonomous medium that spontaneously forms a variety of structures and dynamics similar to those of living organisms.

The Institute has coordinated these phenomena in the wide energy range to create a new energy philosophy incorporated with that referred to as "Zero-Emission Energy". We collaborate with researchers across a broad range of academic fields in Joint Usage/Research Center programs. We hope to develop the breakthrough of energy that will lead the 21st century through the active merging of research in the wide energy range, like the creation of beautiful patterns of fabric interwoven from threads of various forms and shapes.

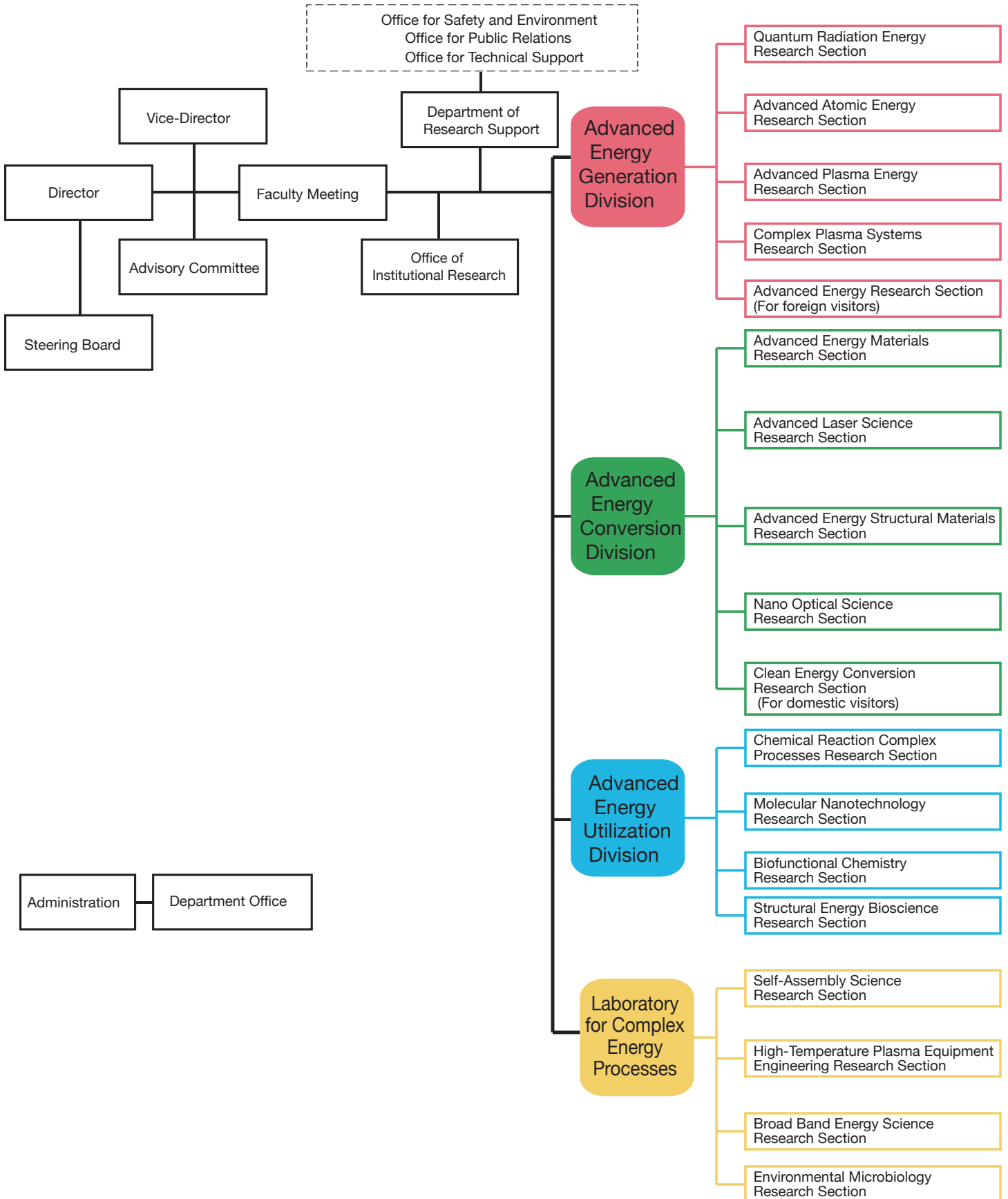
To achieve this end, all of us at the Institute are committed to engaging in extensive discussions, bringing our collective wisdom together, and driving our research and administration under Kyoto University's culture of academic freedom. We look forward to your continued support and cooperation.

A handwritten signature in black ink that reads "Yasuaki Kishimoto". The signature is stylized and cursive.

March 2020

Yasuaki KISHIMOTO
Director
Institute of Advanced Energy
Kyoto University

2. ORGANIZATION CHART



3. RESEARCH ACTIVITIES

3-1. RESEARCH ACTIVITIES IN 2019

Quantum Radiation Energy Research Section

H. Ohgaki, Professor
 T. Kii, Associate Professor
 H. Zen, Assistant Professor
 J. Cravioto, Program-Specific Assistant Professor

1. Introduction

Coherent-radiation energy with wide wavelength tunability, high power and high efficiency is quite promising in the 21st century that is sometimes called the "era of light". The research in this section aims at developing the technology to generate new quantum-radiation energy and apply the radiation in various fields; atomic energy including plasma heating, energy transportation in the universe, material science, material synthesis, electronic device, medical and biological science, etc. Free-electron laser (FEL) is one of candidates for the new quantum radiation, and it is sometimes called the light source of next generation.

2. Free-electron Laser

FEL is regarded as a light source of the next generation because of its wide wavelength tunability where the conventional lasers cannot reach, potential high efficiency, and high power. However, the system is usually much larger and the cost is higher than conventional lasers. We are going to overcome these difficulties by exploiting an RF (radio-frequency) gun, an undulator, etc.

2.1 KU-FEL

The target wavelength of KU-FEL is MIR (Mid infra-red) regime, from 5 to 20 μm . The high power tunable IR laser will be used for basic researches on energy materials and systems. Figure 1 shows a schematic drawing of the KU-FEL system. The KU-FEL consists of a 4.5-cell thermionic RF gun, a 3-m travelling wave accelerator tube, a beam transport system, and a 1.8-m undulator and a 5-m optical resonator. The FEL device now can cover the wavelength range from 3.4 to 28 μm . The maximum macro-pulse energy which can provide is around 40 mJ in a 2- μs macro-pulse at the wavelength of 4.9 μm . The FEL is routinely operated and opened for internal and external users.

Another topic of KU-FEL development is introduction of photo-cathode RF gun, which enables us to generate higher peak power and wider tunable range MIR-FEL. Development of a UV-laser system for illuminating photo-cathode has been completed under collaboration with Dr. R. Kuroda, Researcher of AIST. In FY2014, we have achieved FEL lasing with pho-

to-electron beam generated from LaB₆ cathode. Further study is undergoing to use this operation mode for user experiments.

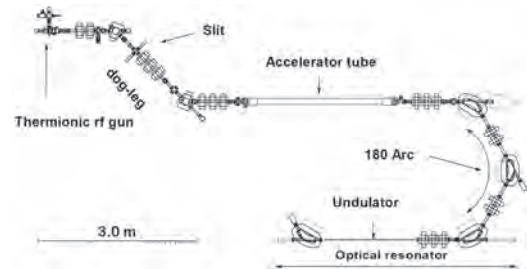


Fig. 1 Schematic drawing of the KU-FEL

2.2 MIR-FEL Application in the Energy Science

Mode-selective phonon excitation (MSPE) is important issue for the bulk solid material to develop the energy saving devices. An MIR-FEL pump, visible pico-second laser probe system has been constructed for measuring the dynamics of phonon vibration which is induced by MIR-FEL irradiation.

High-resolution photoacoustic spectroscopy (PAS) system for solid samples using an MIR-FEL has been also developed and demonstrated.

2.3 THz Coherent Undulator Radiation Source

A new compact terahertz coherent undulator radiation source has been constructed. It consists of a 1.6-cell RF-gun, a solenoid magnet, a magnetic chicane bunch compressor, a triplet quadrupole magnet, a planar undulator, and a laser system for photocathode. Schematic view of the proposed system is shown in Fig 2. In this device, short electron bunches are generated by the photocathode RF gun and the bunch compressor. The electron bunches are injected to the undulator and intense coherent undulator radiation can be generated.

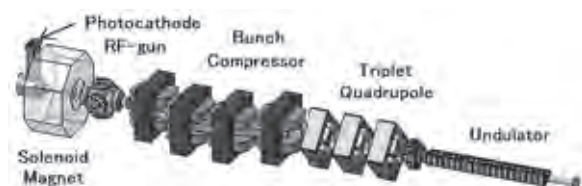


Fig. 2 3D image of THz coherent undulator radiation source.

In order to know the basic performance of the device, detailed experiments have been conducted. As the results, it was confirmed that the device can provide quasi-monochromatic THz radiation from 160 to 650 GHz. Intensity saturation due to space charge effect has been observed. This saturation should be avoided to generate THz radiation with higher peak power. Several methods to mitigate the space charge effect has been investigated. We found that the manipulation of laser pulse shape is a candidate to mitigate the space charge effect and to increase the peak power of the THz-CUR source.

3. Bulk HTSC Staggered Array Undulator

An undulator with strong magnetic field will play an important role in future synchrotron light sources and free electron lasers. We have developing a new undulator which consists of stacked bulk high critical temperature superconductors array and a solenoid magnet. As a next prototype of the new undulator, we have developed new prototype consists of a new solenoid whose maximum field was 6 T and GM cryocooler. Field flatness on beam axis was drastically improved as shown in Fig. 3. Field profile of the undulator for MgB₂ bulk superconductors was also estimated.

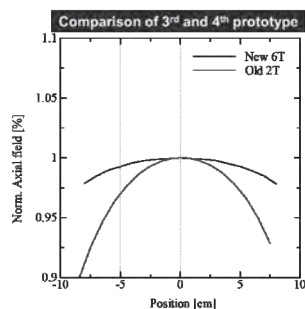


Fig. 3 Comparison of field flatness for old and new prototype..

4. Isotope Imaging for Nuclear Security

A Nuclear Resonance Fluorescence (NRF) method is a powerful tool for investigation not only of the nuclear physics, but also of isotope imaging inside the nuclear waste canisters. We have been developing an isotope imaging technique by using NRF with real isotopes, ²⁰⁶Pb (>93.3%) and ²⁰⁸Pb (>97.8%). The absorption can be measured by sample material and “witness target”.

A demonstration experiment of the NRF-CT imaging by using LCS gamma-ray beam has been carried out at the LCS gamma-ray beamline, BL-1U, at UVSOR-III where 5.528 MeV LCS gamma-rays with a flux of 1×10^8 photons/s can be available. By using NRF absorption method a NRF-CT image has been taken for a sample target CT target which is made of enriched ²⁰⁶Pb and ²⁰⁸Pb rods implanted into an aluminium holder (shown in Fig. 4 (a)). The NRF signals from the witness target (²⁰⁸Pb) were measured by two Ge detectors. At the same time, transmission gamma-rays have been meas-

ured by a LaBr₃(Ce) detector which gives a density distribution of the sample target. The segmented CT reconstruction method has been developed and we obtained clear ²⁰⁸Pb distribution as shown in Fig. 4 (b).

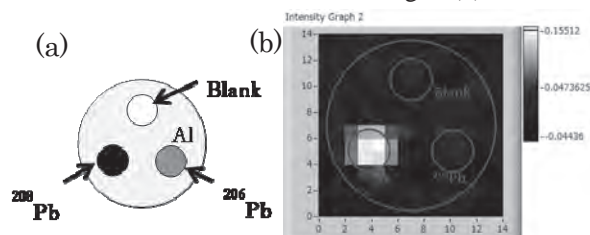


Fig. 4 (a) Sample target, (b) NRF-CT image .

4. Study on Implementation of Renewable Energy

Despite there is general agreement that electrification brings about several benefits to well-being, few works have concentrated on the actual effects of electrification on quality of life (QoL), specifically on the diversity of its dimensions and through non-economic measures. We have been studying diverse electrification schemes (grid extension, centralized hybrid systems and solar home systems) in four rural villages in Malaysia, Cambodia, and Myanmar by using a novel approach with scales on several QoL measures (self-reported QoL, five QoL domains, psychological, physical, social and economic well-being, occupations and active time). With original data surveyed in the villages through a baseline prior electrification and an endpoint several months after, the effects were examined through suitable statistical methods. Overall, we confirmed a positive effect of electrification in self-reported QoL levels, psychological, physical and social well-being, but a certain reduction in economic well-being without any significant difference between these 3 electrification schemes. The findings provide support to the hypothesis of a positive effect on general QoL from electrification, but also suggest with more precision that for specific QoL domains the effect might not necessarily exist or be negative as usually not presumed from a general viewpoint.

Acknowledgment

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Advanced Atomic Energy Research Section

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1. Introduction

Main objective of our research section is to realize advanced energy systems for the sustainable development under global environmental constraints. We have shown a Zero-emission energy scenario based on fusion energy with biomass-based recycling system where biomass waste is converted into liquid fuel or hydrogen. And further we now propose an innovative Negative emission scenario. to isolate CO₂ in the atmosphere by a carbonization process. Our research section focuses on development of hydrogen isotopes fuel circulation system, breeding blankets, fusion material R&D, feasibility study for fusion-biomass hybrid power system, conversion of biomass waste, and fusion neutron generation/measurement. Followings are main research achievements in the fiscal year of 2019.

- Generation of fusion neutron by the cylindrical discharge fusion device and a two-dimensional neutron measurement by imaging plate.
- Develop a novel quantitative analysis method of ¹⁰B for BNCT
- Development of liquid lithium lead droplet system for efficient recovery of hydrogen isotope and heat using a heat and mass-transfer loop.
- Electrochemical approach for impurity monitoring and reduction in liquid tritium breeding material

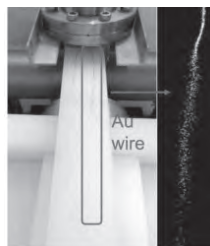


Fig. 1 Gold wire placed by the neutron source (left) and its radiation trace on the imaging plate (right).

2. 2D neutron measurement by imaging plate
 Neutron distribution monitoring in fusion blanket

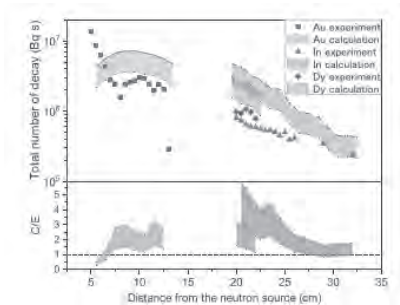


Fig. 2 Comparison of experimental and computed results about the relationship of the total number of decay and the distance.

is a key issue to ensure the self-sufficiency of the tritium fuel. Development of 2D (quasi-3D) neutron measurement is required, so that activation analysis quantified by imaging plate is investigated, using a cylindrical discharge (D-D) fusion device. Several kinds of metal wires and foils (Au, In, and Dy) are placed around a neutron source as shown in Fig.1, where polyethylene blocks are assembled to moderate and shield neutron. The activated sample was placed on an imaging plate and the activity was quantified by scanner to be compared with the estimation by calculation (code: MCNP5) as shown in the Fig.2 where rough agreement was observed.

3. Development of liquid lithium lead droplet system

Lead lithium eutectic alloy (Pb-17at%Li, Pb-Li) is a candidate liquid breeding material with low chemical reactivity and good tritium breeding ratio. Effective tritium recovery method from

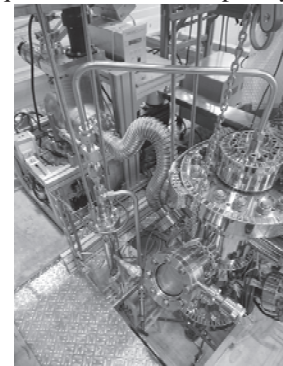


Fig.3: The VST test device integrated to Oroshhi-2 liquid metal test loop at NIFS.

the liquid must be developed for the blanket system with minimal tritium loss. The vacuum sieve tray

(VST) method, tritium recovery from the liquid droplet surface falling in vacuum, is a candidate developed in this section. This fiscal year, on a collaboration work with National Institute for Fusion Science (NIFS) a VST test device (multiple nozzles system) shown in Fig. 3 was integrated to Oroshhi-2 (Liquid metal test loop) at NIFS. Continuous test operation campaign will be performed in the next fiscal year.

4. Electrochemical impurity monitoring and recovery from liquid breeding material

Impurities in liquid breeding material (O in Pb-Li; N, O in Li; HF, H₂O in molten salt, etc.) play significant role on the corrosion of materials. Also controlling hydrogen isotopes are important from the view point of tritium fuel cycle. In this fiscal year, oxygen impurity in liquid lead lithium eutectic is studied to develop the concentration monitoring method based on electrochemistry with compatible chloride molten salt. In an electrochemical cell with LiCl-KCl (59:41 atomic ratio, upper layer) molten salt and liquid Pb-Li (lower) in stainless steel crucible, a glassy-carbon working electrode was immersed and its potential was controlled against Pb-Li liquid (as counter/reference electrode) using a potentio/galvano stat.

The current increases in cyclic voltammogram due to the salt/metal contact and addition of oxide impurity into Pb-Li phase, both are shown in Fig.4, were observed and oxygen impurity transport from Pb-Li to molten salt and the possibility to oxygen removal system using this system is shown. In case of amperometry, bubble formation from the carbon electrode, as well as the weight loss of the electrode were observed, as shown in Fig.5. From these experimental results, the oxygen impurity in Pb-Li is assumed be transferred to molten salt as Li₂O, followed by the diffusion in the salt and oxidation at the carbon electrode surface to form carbon dioxide to be exhausted. Furthermore, for another important impurity in Pb-Li, Polonium which is generated due to the neutron capture reaction of impurity bismuth in Pb, the possibility of

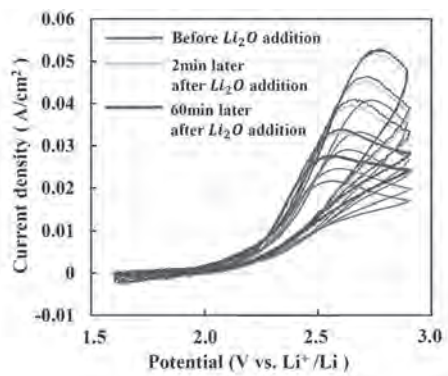


Fig.4: The increase of current due to the oxygen impurity transport from Pb-Li to molten salt (blue), and addition of oxygen impurity into Pb-Li (blue to red).

electrochemical method for its removal is also investigated. Considering the radioactive safety and similarity in chemical behavior, tellurium was used as simulant. Several kinds of metallic working electrodes were tested in LiCl-KCl molten salt contacting with Pb-Li. The behavior due to the tellurium addition to the Pb-Li was monitored. So far, gold electrode is found to be effective to oxidize telluride ion transferred from Pb-Li to molten salt.

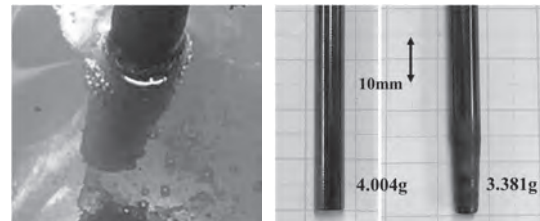


Fig.5: The bubble formation during amperometry(left) and the loss of carbon electrode (right)

5. Development of a novel quantitative analysis method of ¹⁰B for BNCT

Using nuclear reactors for boron neutron capture therapy (BNCT) becomes difficult, while alternative methods to accelerate the development of BNCT research and treatment aiming for higher tumor selectivity and accumulation is a crucial issue. The establishment of a cancer treatment method with an extremely low burden that can be applied to elderly patients is an urgent issue in realizing a society of health and longevity. This work aims to develop a novel quantitative analysis method of ¹⁰B for BNCT. The proposed method is based on detecting α -particles generated from the nuclear reaction between ¹⁰B and thermal neutron, which in principle different from the conventional method that investigating γ -ray. The proposed method mainly depends on using a compact neutron source based on inertial electrostatic confinement fusion device and centrifugal tensioned metastable fluid detector (C-TMFD). When a thermal neutron is hitting a ¹⁰B atom in the detector liquid, the B(n, α) nuclear reaction takes place. The proof of principle and preliminary results of the technique are encouraging.

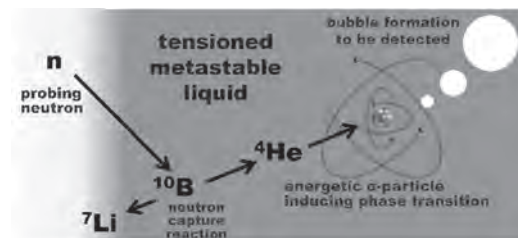


Fig.6: The principle of the ¹⁰B quantitative analysis.

Collaboration Works

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Advanced Plasma Energy Research Section

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1. Introduction

The current subjects of this research section are to study the properties of high temperature plasmas in order to control and improve the plasma energy confinement from the physical viewpoint of nuclear fusion research. The experimental and theoretical investigations for the optimization of the helical-axis heliotron configuration are in progress under the collaboration with groups of international/national institutes and also groups of other universities under the auspices of the Collaboration Program of the Lab. Complex Energy Processes, IAE and the Collaborative Research Program of NIFS (National Institute for Fusion Science).

In this report, remarkable results obtained in the Heliotron J experimental study in FY2019 are reported, focusing on numerical simulation for peripheral plasma dynamics and developments of diagnostic systems; a Q-band super-heterodyne reflectometer for density fluctuation and a radiometer system for electron cyclotron emission.

2. Investigation of heat flux distribution using 3D peripheral plasma transport code

Investigation of the heat flux distribution on the divertor target is one of the essential tasks for fusion devices. The plasma transport in the scrape-off layer (SOL) is dominated by field-aligned transport in the 2D axisymmetric tokamaks. The field-across transport is different between tokamaks and helical devices, and the SOL transport is more complex than tokamak devices because of the inherent 3D magnetic field structure. The 3D effect also appears in the tokamak devices with the application of magnetic perturbation fields to control the edge transport. Therefore, understanding of the 3D effect is the common issue for future reactors regardless of the confinement system. The 3D peripheral plasma transport code, EMC3-EIRENE, has been applied to the Heliotron J to investigate how magnetic field topology affects peripheral plasma transport. The field-aligned 3D grid with fine spatial resolution is required for EMC3-EIRENE calculation. Multiple grids for each magnetic configuration are developed to compare plasma transport among various magnetic configurations.

The heat flux distribution is modeled and compared to the electron density at the core region to investigate the sensitivity of the divertor plasma characteristics to the core plasma. Figure 1 (a) and (b) show the heat flux distribution in the standard configuration on the chamber wall in the low/high density cases, respectively. In the calculations, the diffusion coefficients for the heat/particle flux to the field-across directions are set to be constant. In the high-density case, the peak value of heat flux is decreased and the distribution is wider. In addition, the position of the peak value is shifted in both the toroidal and poloidal directions. These results suggest that the plasma parameter such as the electron density in the confinement region change the balance between the transport along magnetic field lines and across the magnetic field lines, and affect the footprint of the heat flux on the chamber wall.

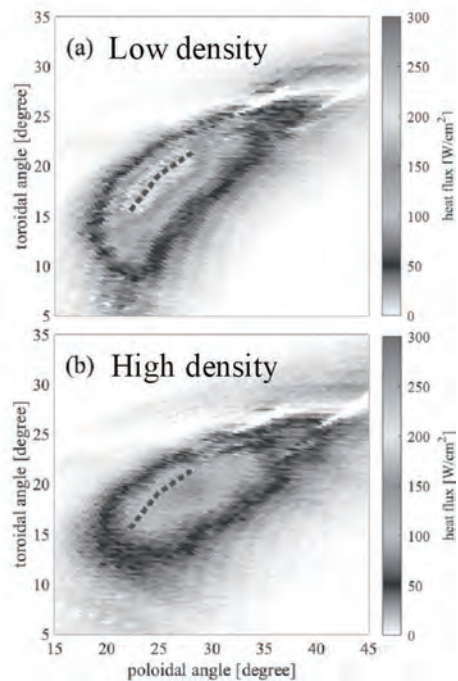


Fig. 1. Heat flux distribution on chamber wall surface for (a) low density and (b) high density cases. The black dotted line in the figure represents the same position on the surface of chamber wall.

3. Development of Q-band super-heterodyne reflectometer for density fluctuation measurement

Density, potential, and temperature fluctuations induce anomalous particle/heat transport in magnetically confined plasmas. We aim to measure electron density and velocity fluctuations using a Q-band super-heterodyne Doppler reflectometer in the Heliotron J device.

The carrier frequency of the reflectometer is employed to be variable in the Q band (33-50GHz), and the microwave is injected as an X-mode. The measurement range in the radial direction is wider than the existing O-mode reflectometer and the density fluctuation more inside the core plasma is possible to measure. The transmitter and receiver of the reflectometer system with a compact, hand-held size are placed inside the vacuum chamber at #10.5 port of Heliotron J, as shown in Fig. 2(a).

We have tried to measure density fluctuations with the new system described above. An initial result is shown in Fig. 2(b). The spectrogram indicates that the broad-band frequency spectrum appears during the plasma discharge. No high coherence with MHD fluctuation was found in this experiment. The observed signal is likely to be turbulent fluctuation, although further study is necessary.

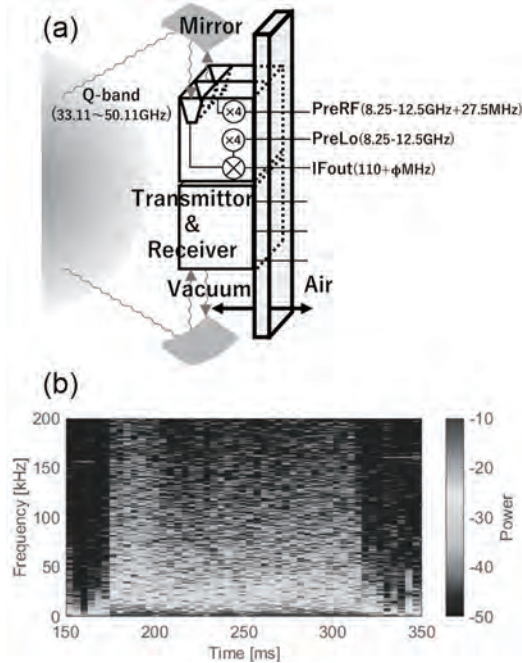


Fig. 2. (a) Schematic view of reflectometer system developed in Heliotron J and (b) time evolution of density fluctuation spectrum measured with reflectometer system.

4. Development of electron cyclotron emission systems for measurement of electron temperature and its fluctuation profiles

Measurement of the electron temperature and its

fluctuation profiles provide us an effective information to study the heat transport in magnetically confined fusion plasmas. Because electron cyclotron emission (ECE) is a phenomenon in the fusion plasmas which is emitted by the black body radiation at the electron cyclotron frequency, measurement of the ECE intensity allows us to evaluate the electron temperature at a local position corresponding to the electron cyclotron frequency. The schematic of the ECE radiometer system for Heliotron J is shown in Fig. 3(a). The conventional ECE of this system (denoted as A) includes 16 channels and can measure electron temperature profile from 58 GHz to 74 GHz which covers from the core to the edge region, and the correlation ECE (CECE) (denoted as B) is composed of CECE-RF and CECE-IF sides. The signals from these two sides share a same source of electron cyclotron emission and thus are possible to estimate electron temperature fluctuation through correlation analysis. As shown in Fig. 3(b), the electron temperature profile has been obtained and compared with data from Thomson scattering system in an electron cyclotron heated plasma. Electron temperature fluctuation levels were estimated in an ECH plasma using a cross-correlation function and a complex coherence function.

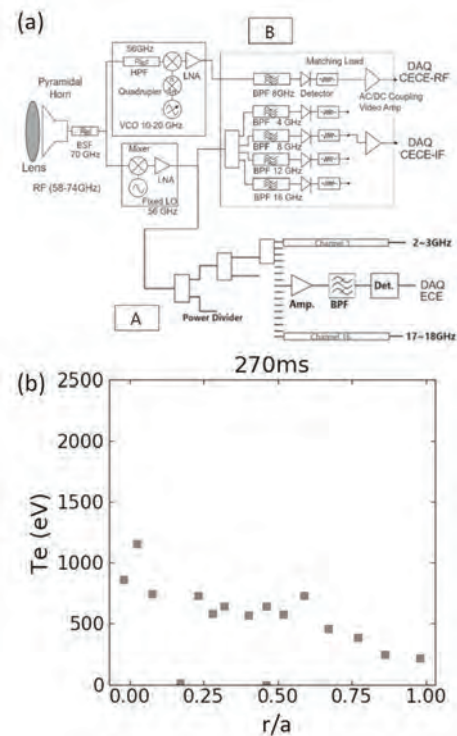


Fig. 3. (a) Schematic diagram of radiometer system for electron cyclotron emission diagnostic in Heliotron J and (b) electron temperature profile measured with conventional ECE system.

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Collaboration Works

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Complex Plasma Systems Research Section

T. Minami, Associate Professor
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 S. Ohshima, Assistant Professor

1. Introduction

Magnetic nuclear fusion energy has some attractive features as a future option for the base-load electrical power source: (1) inherent safety features, (2) no long-life nuclear waste emission, (3) no greenhouse gas emission during the energy production, (4) huge energy density stored in the fuel source (~90 MWh/g for D-T fuel), (5) abundant source availability spreading all over the Earth, and (6) high nuclear proliferation resistance, in terms of both resources and weapons technologies.

Among various issues to be overcome in physics and engineering fields, we have focused on the problems related to the plasma transport and magneto-hydrodynamics. Specifically, determination of a magnetic configuration that can efficiently confine high-density plasma at high temperature with a sufficiently long confinement time and developing diagnostics and control schemes for the high-temperature plasmas in such magnetic fields are regarded as crucial. In these respects, our research section investigates about heating and fuelling, confinement and diffusion mechanisms

and their diagnostics in a magnetic plasma confinement device, named Heliotron J.

Results in FY2019 featured in this report are about the new diagnostic developments.

2. Development of Multi-path Nd:YAG Laser Thomson Scattering System in Heliotron J

We have been developing a multi-path Thomson scattering measurement system [1] that is based on the polarization multi-pass Thomson scattering system [2]. Purposes of the development of Multi-path Thomson scattering system in Heliotron J are as follows. (1) Increase of the scattered light to improve a signal to noise ratio, especially for low-density plasma ($<1 \times 10^{19} \text{ m}^{-3}$). (2) Measurement of the anisotropic velocity distribution of high electron temperature plasma that is heated by the ECH to clarify the effect of the velocity distribution on the plasma transport.

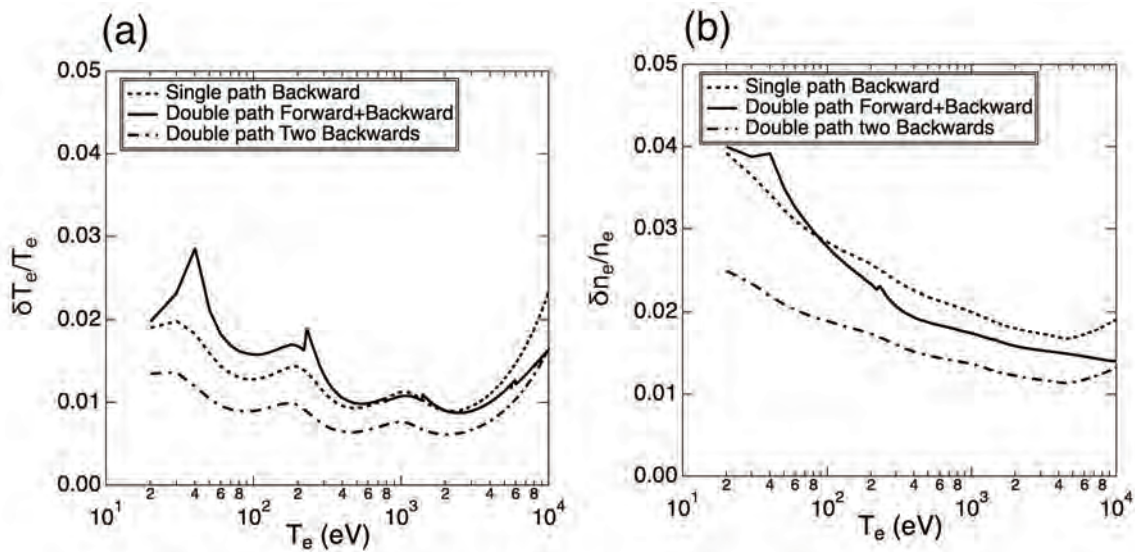


Fig. 1 Estimated errors of single-path and double-path measurements for electron temperature (a) and density (b). The estimation is shown as a function of electron temperature for single path measurement using forward scattered light (dotted line), double-path measurement using forward and backward scattered lights (solid line) and double-path measurement using two forward backward scattered lights (chain line).

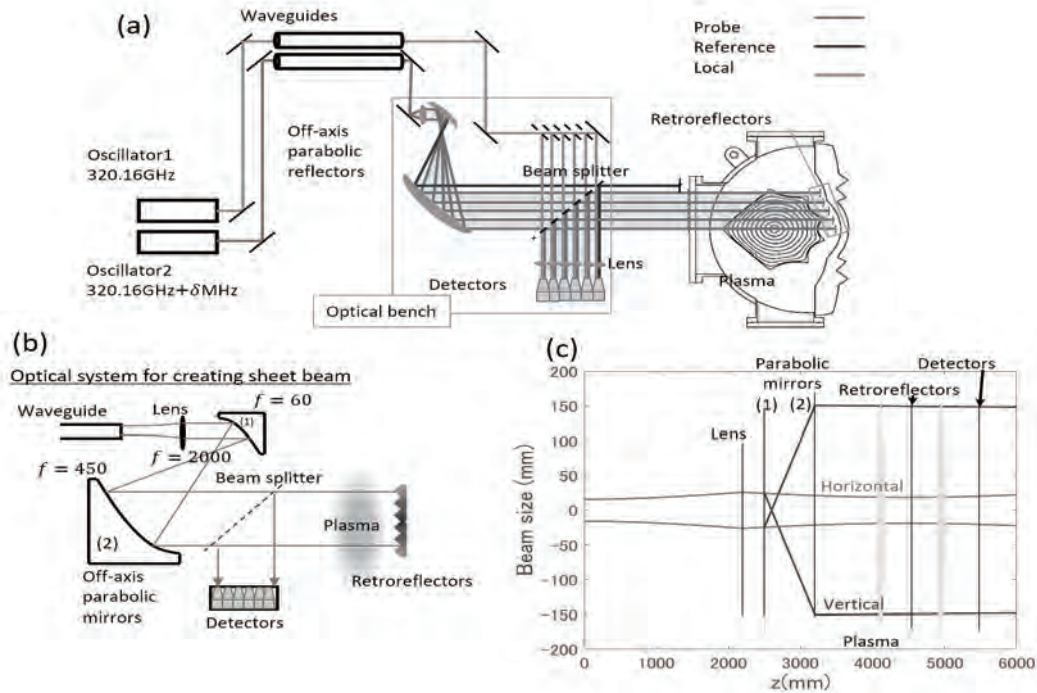


Fig.2 (a)Schematic view of new multi-cahnnel interferometer. (b) optical system for creating sheet beam for multi-channel measurement in new interferometer. (c)Calculated Gaussian beam width in the optical system.

A main issue of the multi-path Thomson scattering design in Heliotron J is a difference of a spectrum between a forward and backward scattering light when we estimate the electron temperature and density values because the laser beam is obliquely injected.

Figure 1 shows the estimated errors of the single-path and double-path Thomson scattering measurements for the electron temperature and density when we use the current polychromator. The solid line shows the error of the double-path measurement for the backward and forward scattering as a function of the electron temperature. The error of the single-path measurement is also shown by the dotted line as the reference. For the electron temperature measurement, the accuracy is expected to increase, when the electron temperature is above ~ 2 keV. However, the accuracy is decreased when the temperature is below ~ 500 eV. For the electron density measurement, the accuracy is expected to increase from ~ 100 eV. These results show that the optimization of the wavelength range of the polychromator is required for the low-temperature measurement.

To measure the anisotropic velocity distribution of high electron temperature plasma in Heliotron J, separation of the backward and the forward signals is essential. The reason why it is difficult to separate the signal waveforms is that the signal has a long tail due to the small decay rate of the scattered light signal waveform. We are designing the double Pockels cells system to achieve the delay time of ~ 100 ns.

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3. Impact of ECH on fast-particle-driven MHD instabilities in Helical Plasmas

A new multi-channel interferometer shown in Fig.2(a) is being developed in Heliotron J for the study of high-density plasma production and sustainment. We plan to upgrade a single-channel FIR interferometer system using an HCN laser to the multi-channel system using double 320GHz solid-state oscillators (Virginia Diode, inc.), which enables a stable, maintenance-free operation of the interferometer.

We finished the design of an optical transmission line in the new system, and the way to produce a sheet beam for multichannel measurement is described here. The schematic view of system for producing the sheet beam is shown in Fig.2(b). The beam is expanded with two off-axis parabolic (OPA) mirrors. By using a set of two OPA mirrors with different focal length ($f=60$ & $f=450$ mm) in a vertical direction, the beam is expanded in the direction, and sheet beam shape can be formed. The calculated beam-width in vertical/horizontal direction is shown in Fig.2(c).

Collaboration Works

長崎百伸, 岡田浩之, 小林進二, 南貴司, Univ. Wisconsin (アメリカ), Oak Ridge National Laboratory (アメリカ), Max Plank Institute (ドイツ), Stuttgart Univ. (ドイツ), CIEMAT (スペイン), Australian National Univ., (オーストラリア), Kharkov Institute (ウクライナ), Southwest Institute of Physics (中華人民共和国), ヘリカル型装置における SOL/ダイバータープラズマに関する研究

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1. Summary

The author spent three months (April 15, 2019- July 14, 2019) as a visiting research scholar at the Uji campus of Kyoto University, hosted by the Professor Hiroshi Sakaguchi.

Here, the author reports about a design and synthesis of new precursors for graphene nanoribbons (GNRs) synthesized through the chemical vapour deposition (CVD) as well as solution processed to Hiroshi Sakaguchi (this work was published in *Chem. Asian J.*, 2019, 14, 4400. So, for more information see this journal).

2. Introduction

Fully π -conjugated 2D structures attract much attention, since they can provide conducting carbon-based nanostructures with holey structures highly suitable for various electronic applications. Utilization of large fully π -conjugated building blocks such as GNRs, which are 1D carbon-based nanowires, is becoming a promising approach to produce extended 2D π -conjugated systems via surface assisted lateral fusion of GNR chains.^{11,12} On-surface bottom-up approaches using chemically designed precursors are regarded as a promising method to produce GNRs with defined edges and widths.¹³ Further, lateral fusion of parallelly aligned GNR led to generation of 2D graphene nanoribbon networks (GNNs).^{11,12} However, it is difficult to efficiently create such sophisticated GNR-linkage structures, since their formation is based on a stochastic surface reaction that requires close proximity between the precursors on the surface.

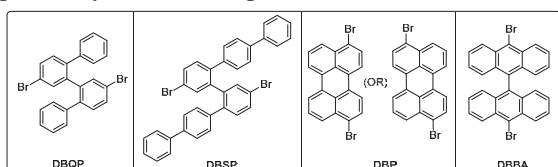


Figure 1. Structure of precursors **DBQP**, **DBSP**, **DBP** and **DBBA**.

In this regard, we have successfully demonstrated on-surface fabrication of a cove-type 2D GNNs with holes, which can be generated by interchain reactions between self-assembled GNRs building blocks on the surface of Au(111) in two zone chemical vapour deposition (2Z-CVD) at elevated temperatures. The GNRs was also

synthesized by the same 2Z-CVD method at lower temperatures using the precursors shown in Figure 1. Further, it can be applied to the TE devices and found that ultra-low thermal conductivity of $0.11 \text{ W m}^{-1} \text{ K}^{-1}$, which is the lowest value among the carbon-based materials as well as inorganic semiconductors.

3. Results and Discussion

The precursors used for the synthesis of 2D GNN is shown in Figure 1 and synthesized according to the reported procedures. On-surface GNRs synthesis was performed by 2Z-CVD under a rotary pump induced vacuum with an Ar flow. The Au(111) substrate was placed in zone 2 of a dual-furnace quartz tube and the precursors was sublimated onto the substrate by passing through zone 1.¹ Independent temperature control of these two separate zones afforded GNRs in high yield without the use of UHV conditions. The advantages of 2Z-CVD include the ability to produce “concentrated radicals” on the metal surface, leading to the formation of high-density, parallelly aligned polymer chains results in self-assembled GNR

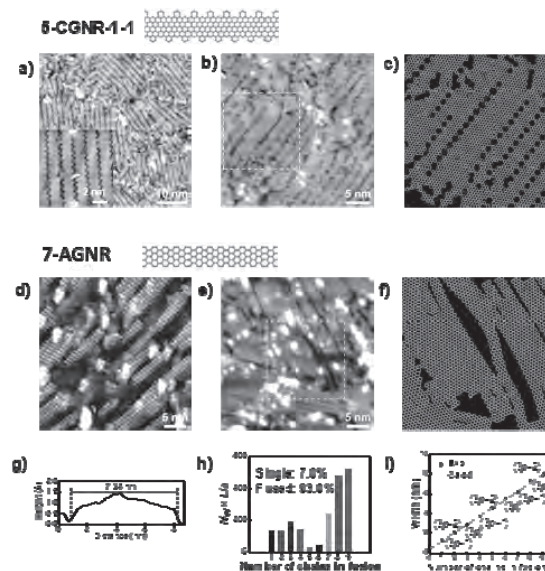


Figure 2. a,b,d,e) STM images of **5-CGNR-1-1** (a) and **7-AGNR** (d). The samples were produced by 2Z-CVD at 500 °C before (a and d) and after (b and e) annealing at 600 °C. The inset in (a) shows a magnified STM image. c,f) Proposed chemical structures of the GNN corresponding to the white dotted area in (b and e,

respectively). g) Cross-sectional analysis of the black dashed line in (e). h) Histogram of the number of chains in fused 7-AGNRs in the STM image (e), with the percentage of single and fused chains shown. The ordinate shows a two-dimensional analogue of the weight-average molecular weight, $N_w \times L/a$, where N_w refers to the counted number of chains in fusion having length L (nm) and a corresponds to the monomer-unit length. i) Experimental and calculated widths of fused 7-AGNRs as a function of the number of chains. The number of carbons in the width of the GNR is categorized into $3p$, $3p+1$, and $3p+2$, where p denotes an integer. The three types of categories are indicated in parentheses at each point.

The material grown by 2Z-CVD at 250 °C on Au(111) using 40 μg of precursor DBSP was subsequently annealed at 500 °C in zone 2 and examined by scanning tunneling microscopy (STM) at room temperature under Ar atmosphere. Densely packed self-assembly of 5-CGNR-1-1s is observed in the STM images (Figure 2a). Remarkably, upon elevating the annealing temperature up to 600 °C, the STM images show fully interconnected 2D network structure confirms the efficient transformation GNR chains into 2D GNNs (Figure 2b). Further analysis of the STM images revealed three kinds of interconnection modes, namely a fusion reaction of parallelly aligned chains to form wider GNRs,^{31,32} orthogonally aligned chains to form terminal–edge junctions,^{33,34} and C–C bond interchain coupling reactions lead to entirely new ladder type 2D-GNNs. Due this interchain coupling between the cove-edged 3- and 5-CGNR-1-1s, periodic holes are generated across the 2D-GNNs.

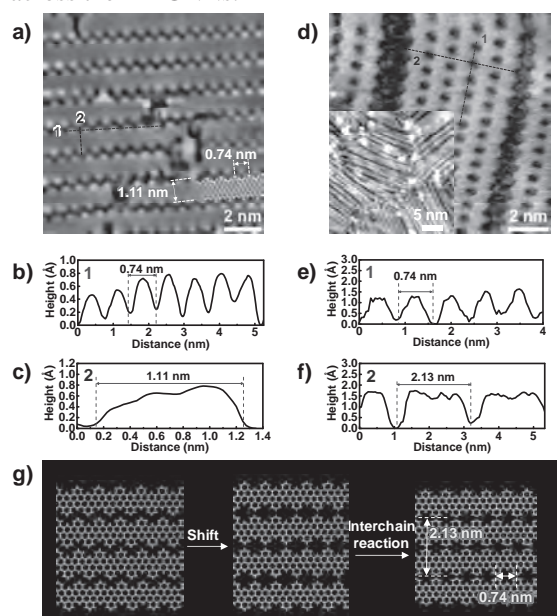


Figure 3. a,d) STM images of 3-CGNR-1-1 produced by 2Z-CVD at 500 °C before (a) and after (d) annealing at 600 °C. Inset of (d) shows a larger area of 35 × 35 nm². b,c) Cross-sectional analysis of the dotted lines in (a). e,f) Cross-sectional analysis of the dotted lines in (d). g)

Schematic representation of the ladder-GNR formation mechanism.

The ladder structure was clearly seen in the 2D-GNNs generated by 3-CGNR-1-1s, which synthesized using the precursor DBQP, as shown in Figure 3. The structural analysis of the ladder-GNRs shown in the STM images was confirmed to match the model (Figure 3). The ladder type 2D-GNNs formation mechanism involving the interchain-coupling of shifting chains is depicted in Figure 3g. Fusion reactions between GNRs produced by UHV deposition have been reported to occur stochastically where GNR chains are in close proximity to each other due to the nonparallel alignment of the chains.^{2,3} Our densely packed, parallelly aligned self-assembled GNRs are able to realize a remarkably high yield of interchain reactions. In addition, the armchair-edged (5-AGNR and 7-AGNR) GNRs were synthesized using the precursor of isomeric mixture of DBP and DBBA, respectively. Upon elevating the annealing temperature to 600 °C, they are also produced 2D-GNNs through the high-yield interchain reactions (Figures 2d-i). The width of the fused 7-AGNRs in the GNN was found to be as wide as 7.34 nm, corresponding to the fusion of eight parallel GNR chains (Figure 2g-i). The observed widths are the widest reported so far for bottom-up fabricated GNRs.² The electronic structure of armchair-edged GNRs has been theoretically predicted to depend on the number of carbons across the width of the GNR (N), categorized into $N = 3p$, $3p + 1$, and $3p + 2$, where p denotes an integer. According to first-principle theory using a tight-binding approximation, armchair-edged GNRs with a width of $3p + 2$ are predicted to have metallic-like characteristics, whereas those with widths of $3p$ and $3p + 1$ have semiconducting characteristics. The bandgaps of 2D-GNNs at defined points in the STM images were measured by scanning tunneling spectroscopy, and based on a rough estimation, the bandgaps of fused GNRs were observed to decrease compared with their single chain counterparts.

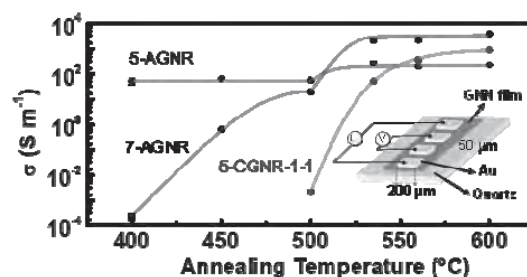


Figure 4. In-plane electrical conductivity (σ) as a function of annealing temperature of five-layer GNR films. The samples were prepared by transferring five layers of GNR films from Au(111) onto a hydrophobic quartz substrate using a gold-etching solution process.

The annealing-temperature dependence of the in-plane electrical conductivity (σ) of five-layer

GNR films were investigated, as shown in Figure 4. For this purpose, GNRs grown on Au(111) were transferred onto a quartz substrate using a previously reported gold-etching solution process.⁴ 5-CGNR-1-1, 5-AGNR, and 7-AGNR have generated at the temperature of 500, 350, and 400 °C, respectively. The electrical conductivity of **5-AGNR**, which is predicted to be metallic-like, was 50 S m⁻¹, whereas those of **7-AGNR** and **5-CGNR-1-1** are semiconducting, were 10⁻⁴ and 10⁻³ S m⁻¹, respectively (Figure 4). The electrical conductivities of these 1D GNRs are in good agreement with the theoretically predicted tendencies. Electrical conductivity of **5-CGNR-1-1** and **7-AGNR** were significantly enhanced by five to seven orders of magnitude, respectively, reaching 900 and 3900 S m⁻¹, upon elevating the annealing to 600 °C (Figure 4). And metallic-like **5-AGNRs** also showed a fourfold enhancement, reaching 230 S m⁻¹ (Figure 3). This kind of electrical conductivity enhancement upon raising the annealing temperature clearly reveals that there is an extension in the carrier path, which can be achieved by the transformation of 1D GNRs to 2D GNNs structure through the fusion and interconnections. The Raman spectra of the GNNs also support the occurrence of such transitions, as spectral changes showing a broadening of G and D peaks and weakening of single chain RBLM peak were observed following the annealing. The macrogap-scale field-effect-transistor properties of 2D-GNNs were also measured and found that GNNs showed higher mobilities and lower on/off ratios compared with those of GNRs.

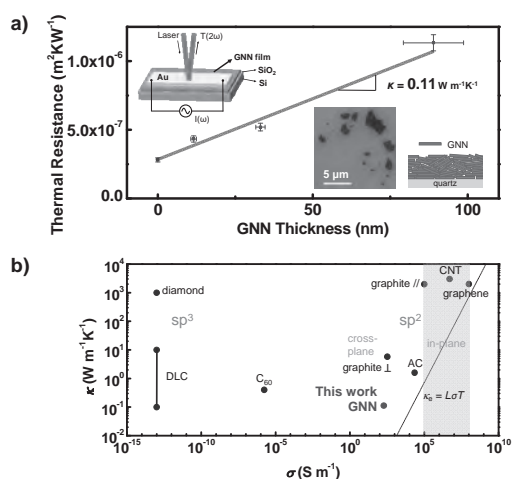


Figure 5. a) Cross-plane thermal conductivity of the GNN based on 5-CGNR-1-1s measured by the thermo-reflectance 2ω method. The bottom right insets show a scanning electron microscope image of a low-density GNN monolayer and the proposed disordered film structure. b) Thermal conductivity (κ) of carbon allotropes as a function of electric conductivity (σ). The dotted line indicates the carrier-induced thermal conductivity (κ_e) derived from the Wiedeman-Flanz law ($\kappa_e = L\sigma T$), where L is the Lorenz factor of $2.4 \times 10^{-8} \text{ J}^2 \text{ K}^{-2} \text{ C}^{-2}$ for free electrons and T is the absolute temperature of 300 K.

To improve the TE properties of GNRs system, different strategies have theoretically been employed; mainly by reducing the thermal conductance while maintaining high thermopower values. One of the best ways to reduce the thermal conductivity of GNRs is by introducing the nanopores in them. The GNR with optimal value of different pore dimensions shows the ZT value 6 times higher than the GNR without pores. Importantly, chevron-type nitrogenated holey (NH) 2D GNRs shows the ZT value up to 1.5 due to the combination of lower phonon thermal conductance and slightly increased the Seebeck coefficient. To this extend, we are trying to validate these predictions by experimentally; here we analyze the TE properties of cove-type holey 2D GNNs experimentally using the model theory for of GNR nanostructures. The cross-plane thermal conductivity of the GNNs was investigated using the 2ω method based on a thermo-reflectance measurement. To investigate the 2D-GNNs formed by 5-CGNR-1-1 films with different thicknesses of up to 89 nm were prepared by repetitive deposition onto a silicon substrate. A plot of the thermal resistance of each sample measured by the 2ω method is shown in Figure 5a. The slope of the thermal resistance plot reveals the thermal conductivity in the cross-plane to be 0.11 W m⁻¹ K⁻¹. This value belongs to one of the lowest thermal conductivities reported so far in carbon-based materials as well as inorganic semiconductors. Because the thermal conductivity was measured in the cross-plane direction, the electrical conductance of 2D-GNNs was also examined in the cross-plane direction and found to be 188 S m⁻¹. Scanning electron microscopy images showed that the GNN film consists of small flakes and AFM images also revealed similar flake structures. Such a disordered structure can be thought to further enhance the reduction of thermal conductivity of the GNN (for more detail please see *Chem. Asian J.*, 2019, 14, 4400).

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Advanced Energy Research Section

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1. Summary

The author spent three months (May. 31, 2019-Aug. 31, 2019) as a guest professor at the Uji campus of Kyoto University, hosted by the Takashi Morii group.

Here the author reports about a special metallo-base DNA based on the fluorescence spectroscopy in Takashi Morii-sensai's group.

2. Introduction

DNA molecule is an considerable interesting material in pharmaceutical technology and nanotechnology due to its chemical stability, ease of synthesis, convenient sequence design[1,2]. The Watson-Crick base pairs, AT and GC, are the fundamental building blocks of the DNA duplex and the basis for the encoding and replication of genetic information. The discovery of metal-mediated base pairs has prompted the generation and application of metallo DNA hybrid duplexes[2] such as ion sensors[3-5], electric transport nanowires[6], and DNA magnets[7-9]. However only some specific nucleic acid duplexes containing metal-mediated base pairs are available and short DNA duplexes that contain up to ten contiguous metalbase pairs have so far been generated[1,10]. The metallo DNA could affect their thermodynamic properties when compared to the corresponding nonmetalated systems.

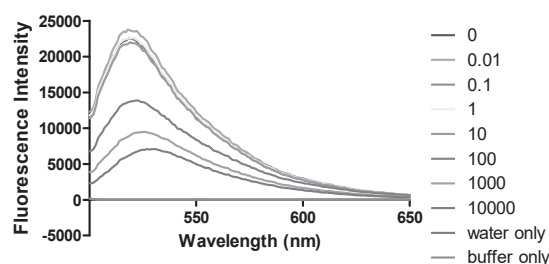
In mercury-mediated T-T base pair(T-Hg-T) structure, mercury could significantly stabilize DNA duplex by stabilize T-T mismatch[3,11] and its binding mode has been demonstrated by different experimental technique(NMR, RDS, CD, UV and MAD) [12-16]. In T-Hg-T structure, Hg^{2+} ion directly binds to N3 atom on thymidine, replacing the hydrogen bonds for base pairs and linking the two thymine residues T:T, making a T-Hg-T monomer characterized at a neutral charge state[1,14]. And these mechanisms are

believed to account for the cytotoxicity of mercury[17,18]. The situation is similar to silver-mediated C-C base pair (C-Ag-C), with the same binding stoichiometry 1:1 and bind to N3 atom of cytosine[4,12]. In addition, long dsDNAs containing metallo-base pairs can be applied for molecular switches [12,13] and new materials such as electronic and magnetic devices. [14] However, long dsDNA containing consecutive C-Ag-C and T-Hg-T base pairs have not been characterized because of the possibility of intrastrand base pair formation induced by metal ions. For further applications, a convenient way to prepare consecutive metallo-base pairs should be developed. We have used a DNA origami scaffold to incorporate DNA strands to maintain the distance between both ends of DNA strands and to manipulate the DNA strands in a topological way.

Here we tried to use the polarization fluorescence to study the behaviors of novel metallo DNA structure.

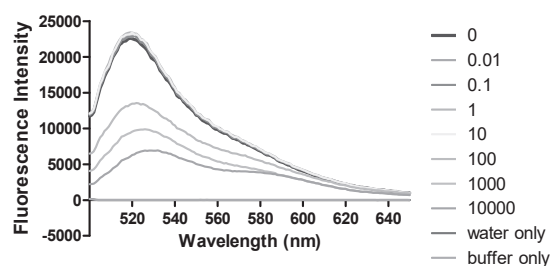
3. Experimental observations

We firstly observed the fluorescence change with different concentration of silver ion, and the DNA sequence was adopted a eleven continuously thymine sequence and labelled with a FAM fluorophore. From the result, we could see the fluorescence was decreased as the increase of silver ion.



We then observed the fluorescence change with the same condition using two almost same DNA sequence which one was labelled with Tamra and another one was labelled with FAM. From the result, we could find there was some FRET phenomenon. The excitation wavelength for FAM was 494 nm and the emission wavelength was around 530 nm. For Tamra, the excitation wavelength was 548 nm and the emission wavelength was around 568 nm. So if the a 494 nm photon was absorbed by a FAM and then it

would be absorbed by a Tamra near it and emit at 568 nm.



This system can be used for the nanoscale construction of nanowires and devices, which can assemble on the surface of DNA nanostructures. Furthermore, this type of observation system is a practical approach for investigating the interaction of various DNA strands and for monitoring the structural changes induced by chemical reactions and environment.

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Advanced Energy Research Section

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1. Summary

The author spent three months (July 1, 2019-September 31, 2019) as a guest professor at the Uji campus of Kyoto University, hosted by professor Hiroshi Sakaguchi.

Here the author reports about an investigation on thermoelectricity study based on enriched semiconducting carbon nanotubes conducted in professor Sakaguchi laboratory.

2. Introduction

Thermoelectricity is important venue to develop novel energy resource such as harvesting electric energy from wasted/natural heat sources. Nanostructuring of bulk inorganic semiconductors has shown particular promise for improving thermoelectric (TE) energy conversion devices owing to the beneficial formation of nanoscale interfaces. However, the best-performing semiconductor are incompatible with applications that require the TE generator to adopt irregular, or even flexible, form factors. Nanostructured organic semiconductors, including single-walled carbon nanotube (SWNT), offer a number of intriguing technological characteristics for TE applications, such as earth-abundant raw materials, low-cost deposition, and flexible form factors. Thermoelectricity (zT) performance is represented by the following equation:

$$zT = \frac{\alpha^2 \sigma}{\kappa} T \quad (1)$$

where α is a Seebeck coefficient, σ is an electrical conductivity, κ is a thermal conductivity, and T is a temperature in Kelvin. Power factor $\alpha^2 \sigma$ is an important parameter to attain high thermoelectricity. In this regard, has gained attentions for this purpose. Especially, semiconducting (*sem*) SWNT has large band gap (1 eV) in which high thermopower α is allowed owing to the lack of density of state between van Hove singularity (vHs). Blackburn *et al.*, reported that larger diameter (d_t) *sem*-enriched SWNT attained high power factor up to few hundreds $\mu\text{Wm}^{-1}\text{K}^{-2}$ with finely tuned doping level of sorted SWNT.[1] However, there is trade-off in powerfactor in which larger- d_t SWNT has good σ exceeding 10^5 S/m yet lowered α below $100 \mu\text{VK}^{-1}$.

Herein, I found power factor of SWNT mat increased as a result of repetitive filtration scheme. Repetitive filtration increases not only the purity of *sem*-SWNT but also lowered carbonaceous impurities, resulting in the highest α of SWNT with similar diameter.

3. Experimental Observations

(1) Materials and Methods

SWNTs which has different SWNT purity has been utilized. As-produced type termed as PSWNT (RN-220 SWCNTs, batch# R26-036, nanotube purity of 30-70%, Nanointegris Inc.) is mainly used, and another type is purified PSWNT termed SPSWNT (SPT-220 SWCNT, batch# PL32-059, nanotube purity of 95-99%, Nanointegris Inc.). Their SWNT diameter (d_t) distribution is 1.3 ± 0.35 nm. Synthesis of Flavin derivatives. *N*¹-dodecyl-4,5-dimethylbenzene-1,2-diamine (2) and FC12 were synthesized via two steps according to a previously reported method.[2] *Preparation of SWNT dispersions*: A mixture of 1 mg of PSWNT and 9.7 μmol of FC12 was added to 4 mL of *p*-xylene dried over 4 \AA molecular sieve. The resulting mixture was exposed to brief bath sonication (5 min, Branson 1510 sonicator, 70 W) for mixing, and further subjected to 1 hr tip sonication [40% power, 18.8 W/mL, probe tip diameter: 13 mm, VCX 750, Sonics & Materials]. During the sonication, the temperature of the sample vials were maintained at 15, 25, and 35 °C by the external water circulator. The centrifugations with different g forces (5 and 30 kg) were conducted by Hanil centrifuge (Korea) at the room temperature. The 80% supernatant was carefully collected for the further measurements. *Preparation of SWNT film*: The SWNT films were prepared by filtration of the dispersed SWNT by filtration of 0.45 μm poresized mixed cellulose ester membrane (Millipore) under reduced pressure. The filtrate was filtered again to produce SWNT mat. Number in SWNT represents number of filtration to produce SWNT mat.

(2) Effect of Filtration on SWNT Purity

Filtration effect on *sem*-SWNT purity has been confirmed by UV-vis-NIR spectroscopy. For this, SWNT mats were prepared on quartz substrates. Fig. 1 displays the 940 nm-normalized spectra after the repetitive filtrations. Clearly, *sem*-SWNT portions centered 940 nm peak remain similar while portion of metallic (*met*)-SWNT near 600 nm decreases. In addition, background absorption attributed to carbonaceous impurity (CI) has decreased as well. This result suggests that the filtration effectively remove residual *met*-SWNT and CI. Moreover, repetitive filtration removes *p*-doping of SWNT, evident by recovered first optical transitions of SWNT.

It is noteworthy that FC12 absorption positioned at 445 nm was completely disappeared, suggesting that filtration step effectively removes residual surfactant on SWNT.

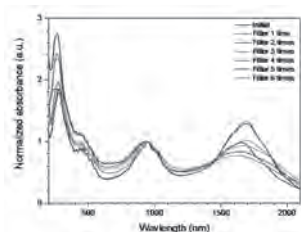


Fig. 1. Normalized UV-vis-NIR spectra of SWNT films on quartz substrate at 940 nm.

(2) Thermoelectric Properties of SWNT Mats

In order to obtain thermoelectric properties, Au electrodes have been fabricated on the SWNT mat. Briefly, a polyimide mask and thermal evaporation has been utilized to make 20 nm-thick Au electrodes for selected area. Those patterned samples were investigated by a custom-made thermoelectric setup, as shown in Fig. 2.



Fig. 2. Photograph of TE measurement for Au-patterned SWNT mat. Outer and inner pairs of electrodes were utilized for current and voltage measurements. Bare probes separated by line drawn by razor blade on the other sides of circular SWNT mat was utilized for temperature measurement.

The measured α was plotted according to number of filtration, as shown in in Fig. 3. Clearly, as increasing filtration number, SWNT mat displays increases α up to five cycles and drops slightly. The SWNT5 which was obtained by 5th filtration showed $\alpha = 645 \mu\text{V/K}$. This value is almost comparable to the highest α of SWNT with similar diameter so far.[1]

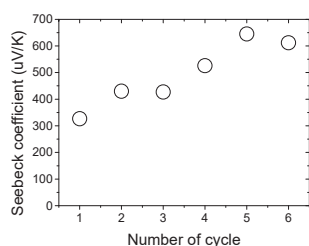


Fig. 3. Seebeck coefficient trend with increasing filtration number.

In order to understand why such high α was obtained, the height images of atomic force microscopy was obtained. The image clearly showed that SWNT mat exhibits dense SWNT without large CI which is typically few tens of nm thick. In addition, length of SWNT has been shortened progressively (data not shown) due to the pore size of the filter. The shortened length seems to result in reduced α by increasing number of junction between SWNT.

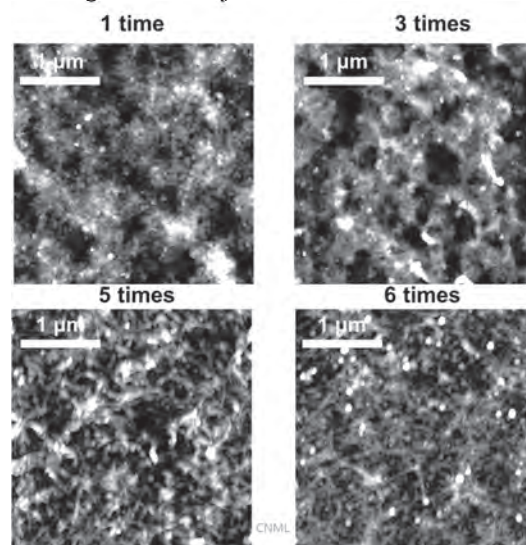


Fig. 4. AFM height images of SWNT mats for respective filtration repetition.

Now, the σ according to filtration number is under investigation, and power factor will be presented soon elsewhere.

Acknowledgement

The author greatly appreciates prof. Hiroshi Sakaguchi and Dr. Takahiro Nakae for help.

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Advanced Energy Research Section

Sadat Mohamed Rezk Khattab, Visiting Research Scholar (Kyoto University Visiting Assoc. Prof.), and (Assoc. Prof. of Microbial biotechnology, Faculty of Science, Al-Azhar University, Assiut campus, 71524 Egypt)

1. Summary

The author spent three months from Oct. 1, 2019, to Dec. 31, 2019, as visiting Assoc. Prof. at the Uji campus of Kyoto University hosted by Prof. Masato KATAHIRA'S laboratory, Structural Energy Bioscience Research Section, Institute of Advanced Energy.

Here the author report on enhance fermentation process efficacy in yeast cells as a top model platform of microbial cell factories using genomic retrofitting the homeostasis' shuttles.

2. Introduction

Owing to increasing demands of energy, therefore the globe had initiated exploits the renewable resources to produce biofuels to mix it with fossil fuels to meet its over needs fuels, besides sustaining its humansphere [1]. Nonetheless, the limited availability of fermentable resources imposes the search to emerge an efficient fermenting process to participate in bridge such a gap from the needs. Despite the idealists of Baker's yeast during either the natural fermentation or even at the harshness of the industrial conditions, but bio-synthesizing glycerol for homeostasis of cofactors and accumulation of acetate decrease fermentation efficiency. At the presence of fermentable sugars with oxygen, there is a need for oxidizing shuttles to re-oxidizes the produced NADH from the oxidation of glyceraldehyde-3-phosphate (GA3P). As a result, the shuttle glycerol-3-phosphate-dehydrogenase (GPD) plays an essential role in this regard with the reduction of dihydroxyacetone phosphate (DHAP) to glycerol 3-phosphate (G3P) to keep this homeostasis. Glycerol synthesized as a by-product of these consequences. Thence, numerous studies regarding the optimization of the oxidation of cytosolic NADH during the fermentation process had published. Such as engineered Baker's yeast by the Pronk group to use external-added acetic acid as an electron acceptor for eliminating

biosynthesis of glycerol during fermentation of glucose under the anaerobic fermenting-conditions after delete GPD genes and integrate a gene of acetylating-acetaldehyde-dehydrogenase ADA [2].

Zelle group had ingested NADPH-dependent alcohol dehydrogenase for tuning the cytosolic cofactor's preferences and integrated with ADA and deleting GPD genes into yeast cells to increase the abundance of NADH. Hence, further activities of ADA enhanced for more of acetate consumption and ethanol productivity [3]. Recently, Chen group reported that the expression of phosphoketolase in yeast cells redirected glucose to acetate after hydrolysis of acetyl-phosphate by endogenous GPP1 and 2. Moreover, it perturbs the sugar-phosphate pools with a significant decrease in xylulose-5-phosphate and fructose-6-phosphate levels at the same time with higher accumulation of glyceraldehyde-3-phosphate and erythrose-4-phosphate. Besides, the increases in the cellular demand for acetate assimilation and respiratory ATP-generation lead to losses of carbons [4].

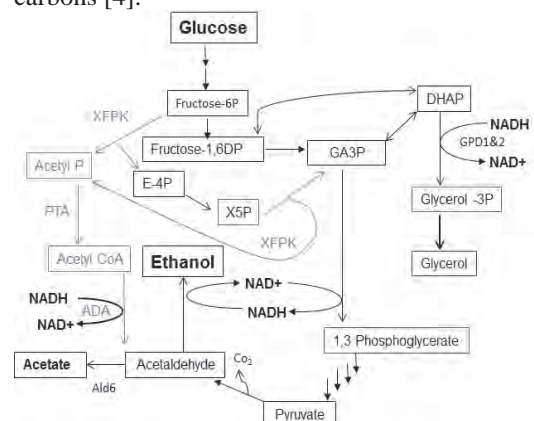


Figure (1): Schematic diagram shows metabolic pathways of the native *Saccharomyces cerevisiae* in black lines integrated with a phosphoketolase pathway (PK-path) in green lines. PK-path includes phosphoketolase XFPK, phosphotransacetylase PTA, and

acetylating-acetaldehyde-dehydrogenase ADA genes.

Sauer group had studied the effects of combining the integration of phosphotransacetylase gene PTA with the ADA gene in previously constructed xylose-fermenting recombinant yeast in a trial for overcoming low ethanol productivity from xylose. Furthermore, the phosphoketolase gene XFPK further integrated with PTA and ADA genes in an additional strain. The engineered strain with PTA and ADA showed preferences and a 25% improvement in ethanol production from the lower accumulation of by-products [5]. Jin's group has also enhanced bioethanol production from corn stover hydrolysate using an engineered *S. cerevisiae* harboring xylose metabolic pathway (XR-XDH-XK) coupled with the ADA gene. The strategy for improving the redox balances with renovates the cofactors (NAD⁺/NADH) had confirmed by the consumption of acetate produced from the pretreatments, with xylose and glucose [6]. Thence, complete retrofits the homeostasis with avoiding accumulates by-products during the fermentation of glucose in the model platform of microbial cell factories through integrating the mentioned strategies and others to reach supreme fermentation efficiency, have envisioned and initiated during our study.

3. Experimental results

(1) Construct expression cassette of phosphoketolase XFPK.

Promoter and terminator were connected to the phosphoketolase gene using the Gibson assembly master mix after amplified each DNA fragment by PCR.

(2) Construct expression cassette of phosphotransacetylase PTA.

With the same method mentioned above, the expression cassette constructed.

(3) Construct the XFPK-PTA module.

The module constructs by combining phosphoketolase cassette with phosphotransacetylase cassette using the Gibson assembly method.

(4) Construct a multiplex pCAS-gRNA-CRISPR system to target the native shuttles for the by-products.

Online tool programs for allocates the highest probability of the on-target sites for CRISPR-Cas 9 used for designing gRNA. The original multiplex-system use as a template for synthesizing the new gRNA scaffold, and then

replaces its original one, by cloning.

(5) The engineered XFPK -PTA yeast.

The homologous recombination of the XFPK-PTA module integrated into a yeast cell by CRISPR- system and the lithium acetate method.

(7) The engineered XFPK -PTA-ADA yeast.

Homologous recombination of linearized ADA-URA3 plasmid carried out complemented in URA3 locus [7].

Finally, preliminary fermentation data at this stage showed betterments in all fermentation process with the efficacy of glucose conversion to ethanol. Currently, we are continuing that retrofitting of homeostasis by re-direct the other cytosolic oxidation of NADH through the acetaldehyde- dehydrogenase-acetylating ADA enzyme. Hence decreasing carbon dioxide CO₂ emission and improve ethanol productivity without reducing the cell formation. The full details of this study are preparing for the publication.

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Advanced Energy Materials Research Section

T. Hinoki, Associate Professor
K. Jimbo, Assistant Professor

1. Introduction

The research activity puts emphases on R&D of the advanced energy materials like SiC composites reinforced with SiC fibers with 10 μm diameter and tungsten composites reinforced with SiC fibers for aerospace, nuclear advanced fission and fusion application utilizing nano-technique. The R&D include development of novel materials, surface modification, and environmental effects including high temperature oxidation and irradiation effects from basic science through engineering. Many collaborative researches are ongoing with domestic and international institutions in US, Italy and OECD.

2. Development of Particle Dispersion Silicon Carbide Composites by Liquid Phase Sintering

Silicon carbide (SiC) is one of very attractive engineering ceramics in particular for severe environment. Silicon carbide composites basically require weak fiber/matrix interphase like carbon (C) or boron nitride (BN). The interphase material and its thickness are keys to determine mechanical properties. However the interphase is the weakest link in terms of environmental effect like oxidation. Precise control of the interphase is also the critical issue in particular for large scale production and affects material cost significantly. The objective of this work is to develop oxidation resistant SiC composites without fiber/matrix interphase

by applying particle dispersion in SiC matrix.

Silicon carbide composites were fabricated by liquid phase sintering (LPS) method. Silicon carbide with BN matrix was formed by mixture of SiC powder and BN powder in LPS composites. Prepreg technique was developed for industrial application under collaboration with industry. Mechanical properties were characterized by various methods including tensile test and fatigue test in air up to 1400 C. Microstructures and fracture surfaces were characterized by FE-SEM.

The BN particle dispersion composites showed excellent high temperature oxidation resistance. Oxidation was limited to near surface. The BN particle dispersion composites don't require fiber/matrix interphase. It decreases material cost significantly. Productivity is also excellent compared to conventional SiC composites. The BN particle dispersion composites didn't break applying 175 MPa following 1 million cycles at 1200 C and 150 MPa following 1 million cycles at 1400 C of fatigue tests in air without any coating. Machinability of BN particle dispersion composites is good. Stress-strain curves of the material fabricated by LPS seems brittle. However it has reliable matrix cracking stress and lower notch sensitivity like pseudo-ductile composites. Figs. 1 show silicon carbide fibers, prepreg and BN particle dispersion SiC composites.

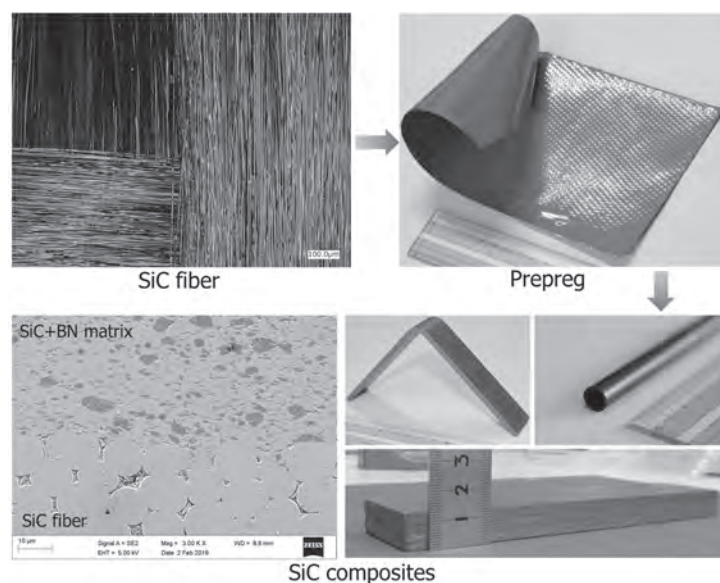


Fig. 1 Silicon carbide fibers, prepreg and BN particle dispersion SiC composites.

3. Ion Irradiation Effect on SiC Composites

Silicon carbide composites are expected to apply for nuclear fission and fusion environments due to stable properties under neutron irradiation. Dimensional change of high purity SiC saturated at around 1dpa in most of temperature range. Microstructure and mechanical properties didn't change above around 1 dpa. Silicon carbide composites consist of SiC fiber, fiber/matrix interphase and matrix. Carbon interphase is a candidate for nuclear application.

It was found that C was unstable at high fluence in particular at relatively low temperature. One of highly crystalline SiC fiber, Hi-Nicalon type-S has small amount of C. Disorder and elimination of C interphase happened following 100 dpa ion irradiation by DuET. Shrinkage of Hi-Nicalon type-S was observed by AFM following 100 dpa ion irradiation as shown in Fig. 2, where high purity SiC matrix swelled. Carbon ribbons observed by FE-TEM for non-irradiated Hi-Nicalon type disappeared following 100 dpa irradiation. It is considered that C ribbons were dissolved in SiC grains. The issues of C interphase and C in Hi-Nicalon type-S were discussed under steering committee of Generation IV International Forum (GIF) –Gas Cooled Fast (GFR) Reactor System-, OECD NEA. Evaluation of high dose irradiation using ion irradiation and development of high dose irradiation tolerant SiC composites will be carried out under PROJECT ARRANGEMENT ON FUEL AND CORE MATERIALS under GIF GFR framework.

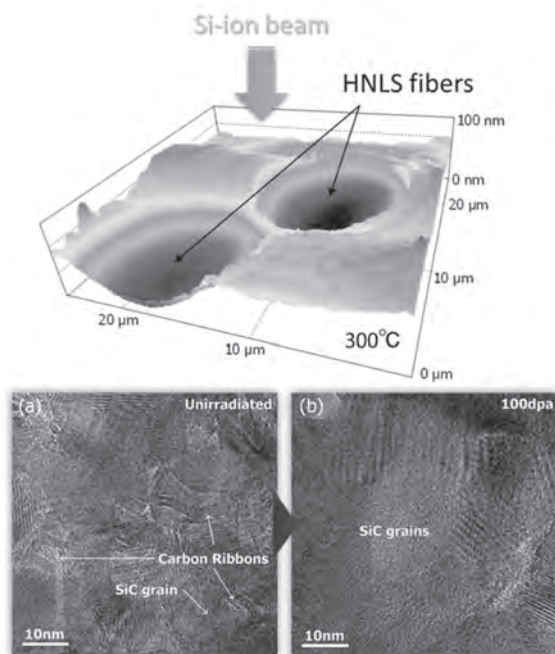


Fig. 2 Irradiation effect on irradiation induced swelling and microstructure of SiC composites.

4. Development of Silicon Carbide Fiber Reinforced Tungsten Composites

Tungsten is a primary candidate material for divertor and first wall. A tungsten material is expected to be used at high temperature due to its extremely high melting point. However mechanical properties of tungsten degrade at high temperature due to recrystallization of pure tungsten above 1000°C. Neutron irradiation also affects mechanical properties significantly. Silicon carbide has very close coefficient of thermal expansion with tungsten. Silicon carbide fibers can be used at above 1000°C under neutron irradiation without significant degradation of mechanical properties. The objective of this work is to develop the tungsten material with ductile behavior under high temperature neutron irradiation environment by reinforcement of silicon carbide fibers.

Tungsten foils or tungsten powders were sintered with silicon carbide fibers by various conditions at 1000~1800°C and ~20MPa. Carbon coated fibers and non-coated fibers were used. Mechanical properties were characterized by tensile test. Microstructure was evaluated by FE-SEM.

Very dense composites were fabricated in case of composites sintered with relatively small tungsten powders less than 1 μm and reinforced with non-coated silicon carbide fibers, however pseudo-ductile fracture wasn't observed. The composites showed pseudo-ductile fracture behavior by fiber pull-out attributed to weak fiber/matrix interfacial strength in case of composites sintered with relatively large tungsten powders or tungsten foils, or composites reinforced with carbon coated silicon carbide fibers as shown in Fig. 3. The pseudo-ductile fracture behavior is independent of embrittlement of tungsten above recrystallization temperature or under neutron irradiation. The magnitude of tungsten can be reduced by replacing with silicon carbide fibers. It can contribute to safety in case of severe accident.

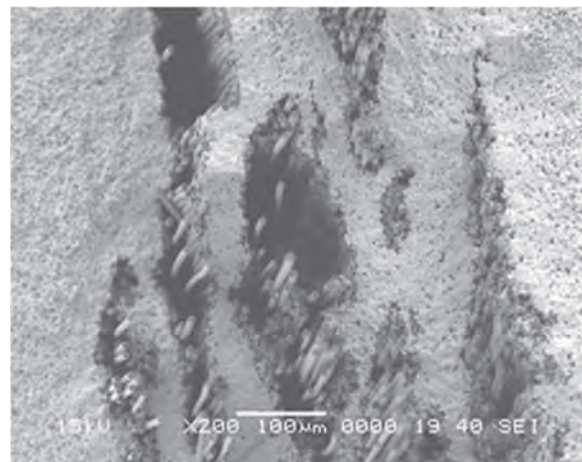


Fig. 3 Fracture Surface of SiC Fiber Reinforced W Composites.

Collaboration Works

檜木達也, Politecnico di Torino (イタリア), Oak Ridge National Laboratory (アメリカ), セラミックス材料の接合強度評価技術開発

檜木達也, OECD NEA, Generation IV International Forum, GFR system

檜木達也, SCK-CEN (ベルギー), 先進事故耐性エネルギーシステムのための革新的被覆管材料

檜木達也, Oak Ridge National Laboratory (アメリカ), FRONTIER 計画 (原型炉ダイバータにおける界面反応ダイナミクスと中性子照射効果)

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Advanced Laser Science Research Section

T. Nakajima, Associate Professor

1. Introduction

Laser is a very powerful tool to synthesize/modify/probe the target materials. Along this line we have been making efforts to develop new techniques to synthesize as well as probe materials which are of great use in energy science. This year we have studied the properties of metal-polymer nanocomposites with a focus on its molecular weight, and developed a simple but efficient technique to detect and also size nanoparticles in bulk water.

2. Influence of polymer molecular weight on the properties of silver-methylcellulose nanocomposites synthesized with a CO₂ laser

Metal-polymer nanocomposites have been attracting lots of interests due to their potential applications. As a new alternative, we have recently demonstrated the rapid in-situ synthesis of metal-polymer nanocomposite films using a CO₂ laser. Among all kinds of polymers cellulose is very abundant natural polymers with nice properties such as biodegradability, biocompatibility, nontoxicity, etc. However, cellulose is insoluble in water and most of the organic solvents, as a result of which it is often used in the forms of bundles such as cellulose nanocrystals/nanofibers. In contrast, the derivatives of cellulose such as methylcellulose (MC) exhibit good solubility in water, and they can be conveniently used for the matrices of metal-polymer nanocomposites.

One of the important and still unanswered questions about metal-polymer nanocomposites is how the properties of metal-polymer nanocomposites are influenced by the molecular weight of matrix polymers. To answer this question, we employ two kinds of MC with different molecular weights (MW=14,000 and 41,000), which are hereafter called MC15 and MC400, and compare the properties of synthesized Ag-MC15/MC400 nanocomposites.

To prepare the nanocomposites we employ the CO₂-laser-based method we have recently developed. Figs. 1(a) and 1(b) show the optical spectra of the synthesized Ag-MC15 and Ag-MC400 films, respectively, with different irradiation times. At the laser power of 1 W the surface plasmon resonance (SPR) of Ag NPs appears at around 400 nm after the 30 sec irradiation for both Ag-MC15 and Ag-MC400 films with some difference that the latter film exhibits a broader spectrum with a longer tail, implying that

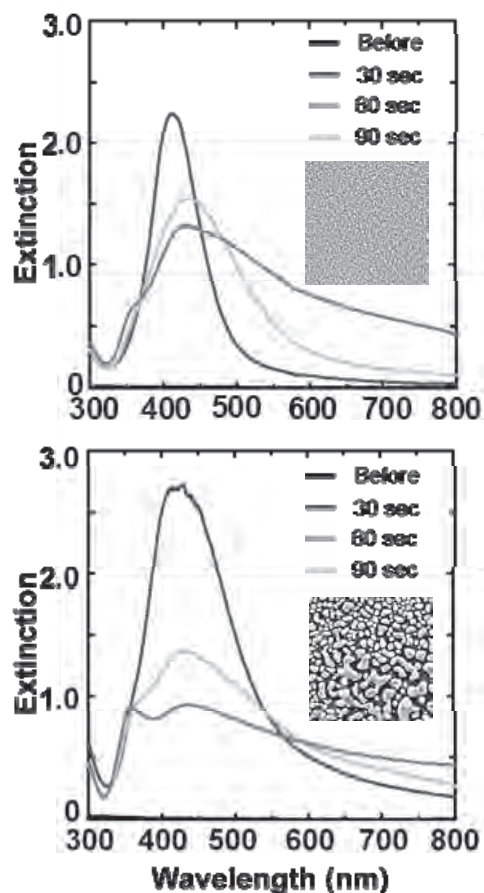


Fig. 1 Optical spectra of the (a) Ag-MC15 and (b) Ag-MC400 nanocomposite films synthesized at the laser powers of 1 W. Insets in each panel show the SEM images after 90 sec irradiation.

that the particle size distribution is broader. For longer irradiation times the difference becomes more obvious. Indeed, the SEM analysis shows that the particle size of Ag-MC400 is much larger after the 90 sec irradiation.

We also investigate the antibacterial property of the synthesized Ag-MC films using the agar diffusion test against *E. coli*. The results are summarized in Fig. 2(a). To be more quantitative, we present the histograms of the inhibited areas, and the results are shown in Figs. 7(b) and 7(c). Interestingly, Fig. 7(b) shows that, for a given laser power the Ag-MC15 film prepared by the shorter irradiation time has a stronger antibacterial property, while for a given irradiation time the Ag-MC15 film prepared by the

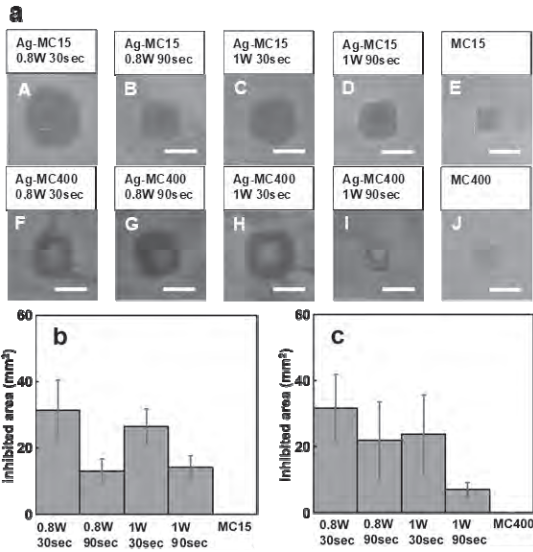


Fig. 2 (a) Results of the antibacterial properties of synthesized Ag-MC nanocomposite films and (b) inhibited area measured from the photos in (a).

lower laser power has a stronger antibacterial property. Similar results are presented in Fig. 7(c) for the Ag-MC400 films. Interestingly, a comparison of Figs. 7(b) and 7(c) suggest that the antibacterial property of the Ag-MC400 films is more or less similar to that of the Ag-MC15 films under the corresponding laser irradiation conditions. To understand this similarity we estimate the number density of Ag nanoparticles and find that they are similar. As for the Ag-MC400 film after the 90 sec irradiation at 1W its antibacterial property is far less than the others, and this can be easily understood that the size of Ag nanoparticles in this case is far larger than the others (inset of Fig. 1(b)), implying that the total surface area is much smaller.

The above results suggest that the choice of the molecular weight of the matrix polymer influences the various properties of the synthesized Ag-MC nanocomposite films, and the similar must be true for any polymer-based nanocomposites.

3. Optical detection of nanoparticles and nanobubbles

Detection of nanoparticles plays an important role in nanoscience and nanotechnology. In particular, in-situ detection of single nanoparticle is very much desired, and several novel optical techniques have been developed. Although some of those techniques are capable of not only detecting but also sizing the nanoparticles, detection is always through a microscopic lens. Moreover, they require that the nanoparticles be in the vicinity of nanostructures to optically or plasmonically enhance the signals. If the nanoparticles detection becomes possible without such nanostructures in a bulk solution, then, we obtain a lot of freedom for the experimental setup.

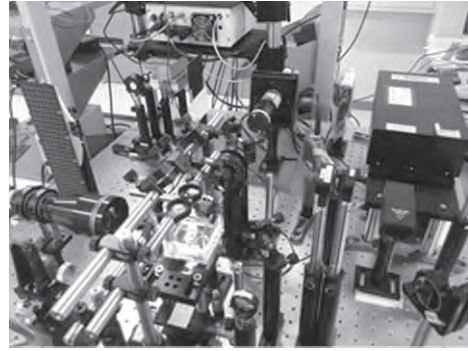


Fig. 3 Experimental setup for the optical detection of single nanoparticles.

We have developed a simple but efficient optical system which can detect isolated nanoparticles of a few hundred nm in a bulk solution without the help of nanostructures from the 10 cm distance. The experimental setup we have developed is shown in Fig. 3. Our technique is essentially based on single-shot laser scattering. The essential difference of our laser scattering technique from the conventional one is that, (1) detection is at the distance of ~10 cm from the target solution, which lifts a lot of experimental constraints, (2) scattering angle for detection is optimized to obtain the enhanced signal by two orders of magnitude, (3) the employed sensor is 2D to detect nanoparticles distributed over the bulk solution, (4) sizing of individual nanoparticles is possible from the brightness of the images.

A sample image is shown in Fig. 4 for the case of polystyrene nanoparticles with three kinds of particle diameters, 500, 750, and 1000 nm dispersed in pure water. We have ensured that, upon irradiation of single laser pulse, the size of individual nanoparticles can be correctly estimated from the brightness of particles. This demonstrates that our detection system will be a convenient workhorse to investigate the time- and position-dependent dynamics of nanoparticles growth, interactions, etc., and if a fast camera and high repetition laser are available, we can study the detailed dynamics with unprecedented time and space resolution.

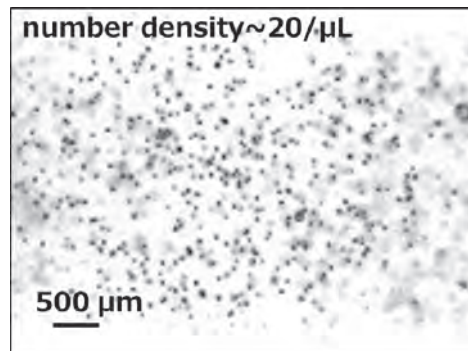


Fig. 4 Optical detection of nanoparticles with a diameter of 500 nm.

Financial Support

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Advanced Energy Structural Materials Research Section

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1. Introduction

Materials development and maintenance management is essential for safe and efficient operation of advanced nuclear energy systems. This section addresses the mission of establishing a maintenance management methodology as well as material R & D for advanced nuclear energy systems such as fusion and fission reactors. Current main researches are as follows:

(1) Plant integrity analysis: The structural integrity of a reactor pressure vessel (RPV) is important for reactor safety and was investigated using three-dimensional computational fluid dynamics (3D-CFD) and the finite element method (FEM). Pressurized thermal shock (PTS) during emergency water cooling, the most severe situation, was focused in the present study. Through this investigation, the magnitude of the risk of the RPV function loss was evaluated and proposed as an indicator available for optimizing the maintenance strategy.

(2) Materials multiscale modeling and data science: Radiation damage processes in nuclear materials take place at a wide variety of time and length scales. So-called the multiscale viewpoint and statistical arguments are required to understand the processes. To do this, modeling effort has been made using several computational techniques complementarily such as molecular dynamics, ab-initio quantum calculations, kinetic Monte-Carlo, rate-equation theory analysis, FEM and CFD.

(3) Irradiation effects on microstructure evolution and properties of materials: High energy particle irradiation leads to the formation of oversaturated interstitials and vacancies. The behavior of point defects is responsible for the evolution of the microstructure, which may cause degradation, (or development), of the mechanical properties of the material. Hence, the elucidation of the behavior of point defects is essential for understanding the mechanisms responsible for the changes in mechanical properties. In our study, the microstructure evolution under high energy particle irradiation has been investigated experimentally and computationally.

2. PTS analysis of a RPV for optimizing the maintenance strategy

The structural integrity of a reactor pressure vessel (RPV) is important for nuclear plant safety. In assessing the integrity of the RPV, one of the most severe situations to be considered is pressurized thermal shock (PTS) during emergency water cooling. Many efforts have been made to understand this PTS, and these efforts assumed symmetric reactor cooling injection. However, once extreme circumstances occur, such as a major earthquake, some of the cooling injections will fail. This failure makes symmetric injection impossible, leading to more serious conditions. In this study, the effect of asymmetric reactor cooling was investigated using three-dimensional computational fluid dynamics (3D-CFD) and the finite element method (FEM). Our results indicate that the most asymmetric injections provide approximately 30% more serious situations than symmetric injections. Additionally, the conventional framework of risk assessment in the architecture with hazard and fragility curves was applied to this issue, and the probability of cooling injection failure, the conditional probability of the RPV fracture, and the probability of the occurrence of RPV fracture were evaluated as a function of the number of injection failures. The probability of the occurrence of a RPV fracture was employed as an index representing the magnitude of the risk of the RPV function loss. Using this

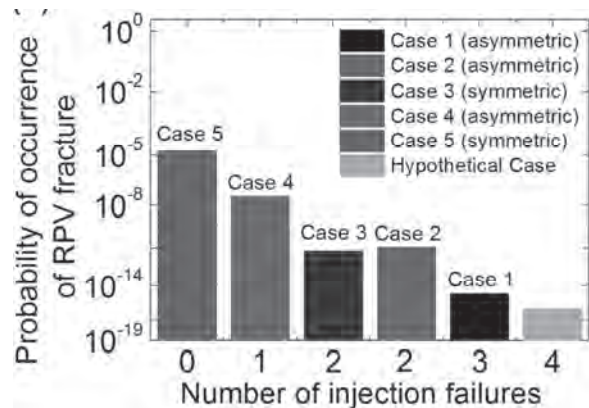


Fig. 1: Probability of an occurrence of RPV fracture as a function of the number of emergency core cooling injection failures in a four-loop RPV.

risk, a methodology to optimize the maintenance strategy was proposed. Regarding the four-loop RPV, the inspection and maintenance of the emergency cooling injection systems are not considered to be the top priority.

3. Statistical arguments towards the development of an advanced embrittlement correlation method for reactor pressure vessel materials

An embrittlement correlation method is one of the most important techniques used to ensure the integrity of pressure vessel steels in nuclear power plants. In Japan, the embrittlement correlation method is being addressed in accordance with the Japan Electric Association Code (JEAC 4201), which was developed using actual measured data on the irradiation embrittlement of pressure vessel steels. In the present study, to develop more reliable methodologies, statistical arguments were made concerning the embrittlement data. With regard to a set of residual data defined in JEAC 4201 as a collection of differences between the measured and calculated ΔDBTT (ductile-to-brittle transition temperature shift) values, a statistical relationship between the population and samples was found, and then, the sampling errors in the mean values of the residuals were identified as key for establishing a more reliable correlation method. Using this relationship, it was noted that when predicting the amount of irradiation embrittlement of pressure vessel steels in a particular plant using the JEAC 4201 correlation method, the deviation associated with sampling errors needed to be corrected. Based on this finding, a more appropriate interpretation was found for the so-called MC correction in JEAC 4201, and moreover, a new correction method was developed within the framework of *Bayesian* estimation. This new correction method will be useful for establishing further advanced methodologies to manage irradiation embrittlement using the probabilistic risk assessment approach.

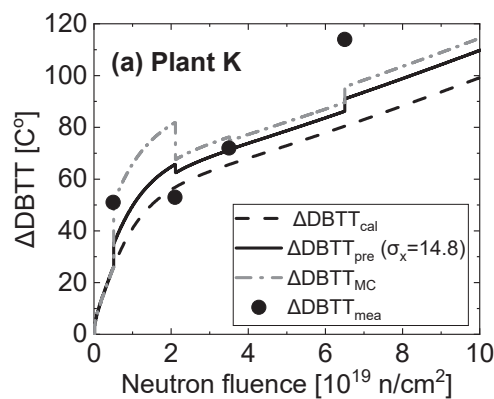


Fig. 2 Time evolution of the DBTT changes for the example plant. Prediction and correction methods are developed and applied to this evaluation.

4. Irradiation effects on microstructure evolution and properties of materials

Tungsten (W) is considered to be the primary choice for the plasma facing materials (PFM) in fusion reactors due to its attractive combination of properties such as high melting point, good thermal conductivity, high creep resistance, good high-temperature strength and low vapor pressure. We have investigated the irradiation effect of tungsten (W), which is a candidate material for fusion divertor, using an ion accelerator (DuET: Fig. 3). We found that the microstructure evolution under ion irradiation depends on the crystal orientation using W single crystals with {001} and {011} surface orientation for ion-irradiation (Fig. 4). Defect zone depth is deeper in {001} crystal than in {011} crystal. The mechanism has been discussed with DFT, MD, and so on. The knowledge obtained in this study is fruitful for fusion divertor design and integrity. Moreover, we performed a systematic theoretical study of the interactions between transition metals (TM) elements and point defects in bcc W using density functional theory (DFT) calculations. The effects of transition metals elements on the microstructure evolution was discussed.

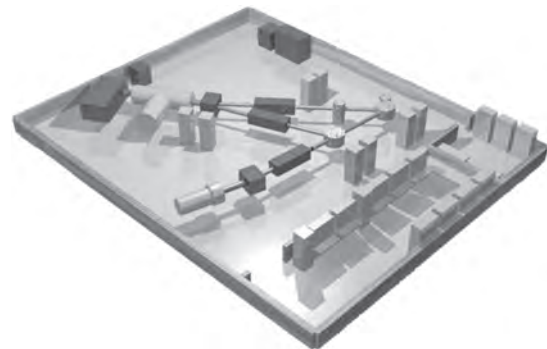


Fig. 3: Ion-accelerator (DuET)

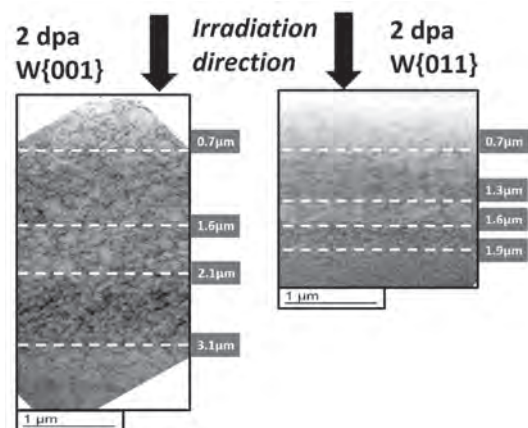


Fig. 4: TEM micrographs of W single crystals after 6.4 MeV Fe^{3+} ions.

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2. Others

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Nano Optical Science Research Section

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1. Introduction

We are working on basic and applied research of nano-materials from a viewpoint of optics and material science. Our research aims at exploring new physical and chemical phenomena leading to applications of novel nano-materials including carbon nanotubes, layered transition metal dichalcogenides, perovskite for efficient utilization of light energy and development of future optoelectronic devices with ultra-low energy consumption. Followings are main research achievements in the year of 2019.

1. Continuous Control of Excitonic Valley Polarization in Monolayer WSe₂ by electrostatic doping

A “valley” is an electronic degree of freedom in momentum space, and its potential applications as information carriers in future electronics or optoelectronics devices are called valleytronics. Monolayers of transition metal dichalcogenides (1L-MX₂) (M = Mo, W; X = S, Se, Te) have recently emerged as promising two-dimensional (2D) materials for developing valleytronics because they have hexagonal lattice structures similar to that of graphene but are semiconductors with finite direct band gaps in two inequivalent +K and -K valleys related by a time-reversal operation in the 2D hexagonal Brillouin zone. Because of the reduced screening resulting from the atomically thin 2D structures of 1L-MX₂, their excitons, which are mutually attracting electron-hole pairs that interact through Coulomb interactions, have extremely large binding energies and dominate their optical responses even at room temperature. In addition, the strong spin-orbit interactions in these materials give rise to large spin splitting in the valence band. This large valence spin splitting and a lack of inversion symmetry in these materials lead to spin-valley coupling that enables exclusive access to the excitonic valley pseudospins ($|+K\rangle$ or $|-K\rangle$) with right- or left-circularly polarized photons. These unique characteristics of 1L-MX₂ have provided unprecedented platforms for the study of valley-exciton physics in 2D systems, as well as offering opportunities for developing future optoelectronic devices using the excitonic valley degrees of freedom.

Here, enhancement and continuous control of the excitonic valley polarization in electrostatically doped

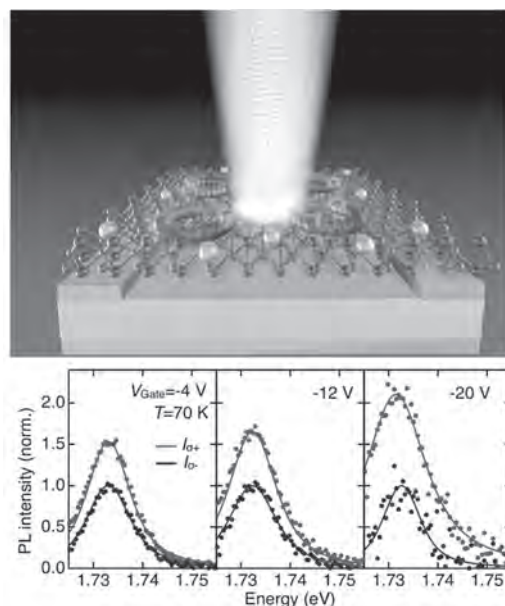


Fig. 1 Schematic of control of excitonic valley polarization (upper panel). External bias dependence of valley polarization monitored by polarization resolved photoluminescence (PL) spectra.

monolayer WSe₂ were demonstrated. Under excitation with circularly polarized light, 20% valley polarization of excitons around the charge neutrality condition at 70 K is increased to 40% by modulating the electron/hole density up to $2 \times 10^{12} \text{ cm}^{-2}$. This increase originates from slow valley relaxation for neutral exciton between the K and -K valleys owing to screening of long-range e-h exchange interactions by doped carriers. The gate-dependences of the exciton valley polarization at various temperatures are reproduced by theoretical calculations, which holds potential for next-generation valleytronic devices continuously controlled by an applied bias voltage.

2. Experimental Evidence of the Anisotropic Triions in Atomically Thin Two-dimensional ReS₂

Since the discovery of atomically thin black phosphorous (black phosphorene), atomically thin 2D materials with anisotropic crystal structures, such as GeX (X=S, Se), SnX (X=S, Se), have been extensively studied as a new research direction for 2D materials.

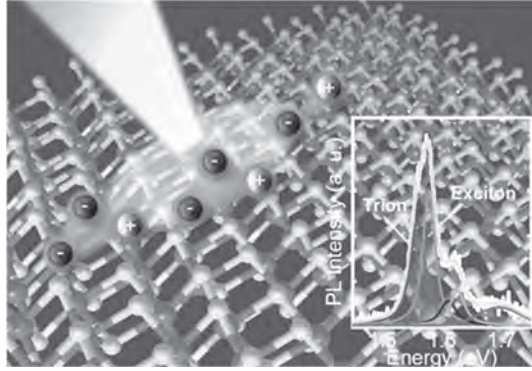


Fig. 2 Schematic of exciton and charged exciton generated in monolayer ReS₂. Inset shows photoluminescence spectra.

Such atomically thin 2D materials exhibit the anisotropic carrier transport and optical properties owing to the anisotropic electronic structures, which provide the novel characteristics of linear dichroism, valley selective excitation by linearly polarized light, and polarization-sensitive photodetectors from the viewpoints of optical physics and device applications. Contrary to the isotropic structure MX₂, ReS₂ is a layered material with a reduced symmetry because of the weak interlayer coupling from the distorted 1T structure, which imparts highly anisotropic optical absorption and photoluminescence (PL). A field-effect transistor (FET) with highly anisotropic carrier transport and polarization-sensitive photodetectors is also demonstrated in ReS₂. Moreover, the ReS₂ shows superior stability in the ambient condition, which is much different from the well-studied anisotropic black phosphorous (black phosphorene). The three-particle bound states of charged excitons (trions) with a charge degree of freedom dominate the optical responses in the atomically thin 2D MX₂. The experimentally observed stable trions with a large binding energy (20-36 meV) in the atomically thin monolayer 2D transition metal dichalcogenides MX₂ with an isotropic crystal structure have been extensively studied. However, the trions in atomically thin 2D materials with an anisotropic crystal structure, being a new platform for studying many-body physics in the quasi-one-dimensional (1D) systems, have not yet been completely understood, especially in ReS₂, even though the many-body physics in the quasi-1D system would show the significant differences arising from the dimensionality dependent dielectric screening in the 2D and in the 1D carbon nanotubes. Moreover, the three-particle bound states of trion in the quasi-1D ReS₂ would also provide an outstanding platform in the practical optoelectronic applications.

Here, we demonstrated the first experimental observation of the negatively charged excitons (negative trions) in a few-layer ReS₂ with FET structures by tuning the gate voltages. The new PL peak that can be observed below the lower energy side of neutral excitons

in the electron doped region can be attributed to the emissions from the negative trions. The polarization dependence of the PL intensity suggests the presence of strongly polarized emissions from the trions, which reflect the anisotropic natures of the trion wavefunction. The trion binding energy is strongly dependent on the layer thickness, and the estimated trion binding energy of 1L-ReS₂ is ~60 meV, which is more than twice larger than that of other typical isotropic 2D materials MX₂. Further, the enhancement of the large binding energy reflects the quasi-1D natures of trions in the atomically thin ReS₂.

3. Recycled Utilization of a Nanoporous Au Electrode for Perovskite Solar Cells

We also successfully developed a new and facile approach to deposit a nanoporous Au film contact electrode using a dry transfer process in perovskite solar cells (PSCs). The high specific surface area of the nanoporous Au electrode results in tight contact with hole transport layer of 2,2,7,7-tetrakis(N,N-di-p-methoxyphenylamine)-9,9-spirobifluorene (spiro-OMeTAD). This enables a high PCE of 19.0% with a negligible hysteresis of photovoltaic performance in PSCs. The superior properties of the nanoporous Au electrode facilitate recycling, where the same electrode can be used more than 12 times in PSCs. This significantly reduces device fabrication cost and noble Au metal consumption in PSCs. Flexible PSCs (fPSCs) that use nanoporous Au films may be able to sustain a much higher bending durability of ca. 98.5% after 1000 bending cycles in comparison with that measured in the usual fPSCs based on the evaporated Au. This is attributed to the nanoporous structure that hinders crack generation and propagation in nanoporous Au films. This study demonstrates the following: the aforementioned novel simplified deposition process, the recycling of the electrode in PSCs using nanoporous Au electrode films, and PSC devices performance.

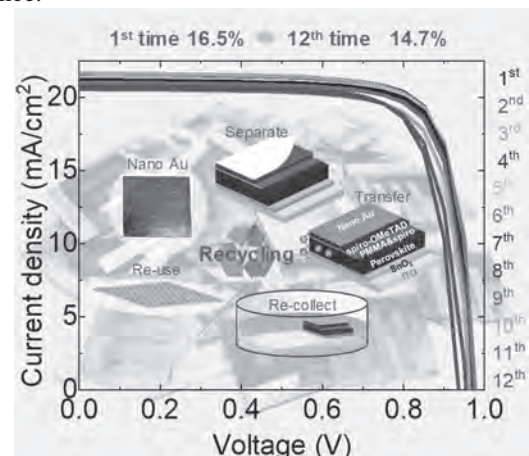


Fig. 3 Schematic of recycle utilization of nano-porous electrode for perovskite solar cell, and its photovoltaic performance in recycled utilization of electrode.

Collaboration Works

松田一成, University of Bordeaux, 単一ナノ物質における先端分光

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1. Grant-in-Aid for Scientific Research

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松田一成, 挑戦的研究(萌芽), 高次データ科学による原子層物質のバレースピノ制御

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Clean Energy Conversion Research Section

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1. Introduction

In order to achieve full-scale utilization of renewable energy, such as solar and wind powers, it is indispensable to establish power leveling technologies. High-capacity and high-safe rechargeable batteries are the most desired devices for this purpose. In many of rechargeable batteries, solid state ionic conductors are often used as the electrolyte and/or the electrodes.

For improving solid state ionics devices, it is important to understand the electrode reactions, which are often main causes for the degradation of the device performance. Various electrochemical measurement techniques are applied to investigate the electrode reactions. However, conventional electrochemical measurements can give us only indirect information on the electrode reactions. The introduction of spectroscopic measurements, which can “visualize” the reaction under the device operation, is helpful for deep understandings of the electrode reactions.

Our research group is developing *operando* spectroscopic techniques for investigating solid state ionics devices by applying synchrotron X-ray. In this report, our recent results obtained with synchrotron X-ray *operando* measurements of all-solid-state batteries (ASSBs) are introduced. The rate-determining processes in ASSBs are discussed based on the results of direct observation of the electrode reactions.

2. Reactions in all-solid-state batteries (ASSBs)

ASSBs are expected as a new generation batteries, which can achieve safety operation, high output power and high capacity [1-3]. In this type of batteries, smooth and homogeneous reactions in the electrodes are required. For instance, in a composite electrode consisting of electrode active material and electrolyte particles, it is considered that the reaction kinetics is influenced by various mass transport processes, such as transport of ion in the electrolyte particles, transports of ion and electron in the active material particle, and charge transfer at the electrode/electrolyte interface. If one or some of these mass transport processes would be very slow, ion or electron could not be sufficiently supplied to a part of active materials, resulting in the deterioration of the capacity and output power. Moreover, such an inhomogeneous reaction in a composite electrode may cause overcharge or overdischarge of the active material, and lead to fatal degradation of the

durability and the safety. Therefore, in order to develop batteries having sufficient performance, it is necessary to clarify causes for the reaction distribution formation and to optimize the electrodes and operation conditions.

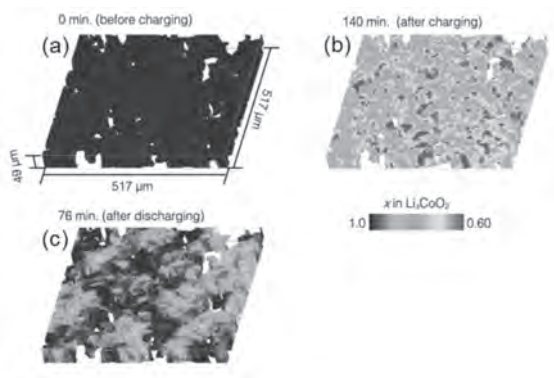
In this study, the computed tomography X-ray absorption fine structure (CT-XAFS) technique [4, 5] was employed to visualize the 3-dimensional distribution of the state of charge (SOC) in an ASSB electrode under the operation.

3. CT-XAFS measurements of ASSLIBs

CT-XAFS is an analytical technique to combine three-dimensional computing tomography imaging with X-ray absorption fine structure measurement. This technique enables us to non-destructively evaluate three-dimensional distribution of chemical and electronic states of specimen for relatively large observation area within reasonably high position and time resolutions. In this work, Li_xCoO_2 (LCO)- $\text{Li}_{2.2}\text{C}_{0.8}\text{B}_{0.2}\text{O}_3$ (LCBO) | LCBO | poly(ethylene oxide) (PEO) - based polymer | Li, which was developed by Okumura *et al.* [6], was chosen as an example of ASSBs, and the reaction distribution in its composite cathode was investigated. The Li content x in Li_xCoO_2 , *i.e.* the state of charge (SOC), was determined from the peak top energy of the Co K -edge XAFS spectrum [7]. The size of the observation area was $630 \times 517 \times 46 \mu\text{m}^3$ and the positional resolution was *ca.* $3.1 \mu\text{m}$. The time required for obtaining one three-dimensional (3D) SOC map was approximately 25 min..

4. *Operando* observation of reaction distribution in an ASSB

The ASSB cell was charged/discharged with a current of $100 \mu\text{A}$ and the cut-off voltage of 2.0-4.35 V. CT-XANES measurements were repeated at every 30 min. or 1 h during the charge/discharge. The observed capacities were 57 and 52 mAh/g for charging and discharging, respectively. From these capacity values, the Li contents (x in Li_xCoO_2) after charging and discharging were estimated to be $x = 0.79$ and 0.98 , respectively. If the cell is charged to the rated capacity (100 mAh/g in this work) as intended, the average Li content should be $x = 0.64$. But the Li content evaluated from the electrochemical response ($x = 0.79$) was much larger than this value. This indicated that some of active materials in the composite electrode were not fully



charged and an inhomogeneous reaction distribution was formed during charging. On the other hand, the most of active materials seemed to be fully discharged after discharging, because the Li content was recovered nearly to the original value ($x = 1.0$).

Figures 1(a)-(c) show 3D SOC maps obtained from CT-XANES measurements before and after charging, and after discharging, respectively. The colored and transparent areas correspond to the active material and the solid electrolyte/void, respectively. The red/blue areas indicate the fully charged/discharged areas. The Li contents after charging/discharging were estimated to be $x = 0.77$ and 1.0 , respectively, which were in good agreement with those estimated from the charge/discharge capacities, *i.e.* $x = 0.79$ and 0.98 . This demonstrated that CT-XANES technique can evaluate the reaction distribution in an ASSB composite electrode three-dimensionally and quantitatively.

From the 3D SOC map, two-dimensional (2D) SOC map can be extracted at any desired cross sections. Representative results in the thickness and the in-plane directions after charging were shown in Figs. 2(a) and (b), respectively. These figures clearly showed that the charge reaction inhomogeneously progressed both in the thickness and the in-plane

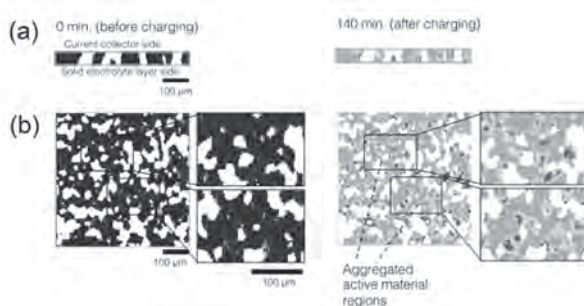


Figure 2. Representative cross-sectional 2D SOC maps before/after charging (a) in the thickness direction and (b) in the in-plane direction.

directions.

However, in the thickness direction (Fig. 2(a)),

the SOC is appeared to be random, and there seemed to be no monotonical change in this direction. This indicated that neither ion transport through solid electrolyte particles nor electron transport through active material particles were rate-limiting in this composite cathode under the applied charge/discharge conditions. On the other hand, in the in-plane direction (Fig. 2(b)), relatively higher charged regions (red regions) tended to exist near the outside of active material particles, which was thought to be near the solid electrolyte. Contrarily, relatively lower charged regions (blue regions) tended to be present inside the active material regions. From these results, we can infer that the ion transport through active material particles is slow in the composite electrode. Considering the average particle size of LCO ($\sim 10 \mu\text{m}$), it was considered that the SOC inhomogeneity in Fig. 1(b) did not occur within one active material particle but within aggregated active material particles. It is thus concluded that the slow ion transport through active material particles is caused by the large interfacial resistance between LCO particles.

5. Summary

In this work, *operando* 3D evaluation of reaction distribution in an ASSB composite electrode was performed by applying CT-XAFS. As results, it was found that the primary rate-limiting process was the delay of the ion transport through active material particles. This work clearly demonstrated that synchrotron X-ray *operando* spectroscopic analysis can be very powerful tools in understanding the factors responsible for reactions and ion/electron transports in solid state ionic devices.

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Clean Energy Conversion Research Section

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1. Introduction

Behaviors of lithium materials which produce tritium fuel through the nuclear reactions of ${}^6\text{Li}$ (n, α) T and ${}^7\text{Li}$ ($n, n'\alpha$) T are significantly important issues in development of fusion blanket systems. However, techniques to analyze lithium distribution in materials are limited. The soft X-Ray emission spectrometer (SXES) system in Institute of Advanced Energy (IAE), Kyoto University was applied to analyses of Pb-Li and the related materials.

Regarding development activities of fusion blanket systems, various engineering issues are being studied under collaborative programs between universities and National Institute for Fusion Science (NIFS). To accelerate blanket design studies by reflecting the results in the collaborative studies, numerical calculations of blanket performances have been started for several proposed configurations.

2. Soft X-ray analysis on fusion blanket related materials

The soft X-ray emission spectrometer (SXES) in IAE, Kyoto Univ. can be used to measure not only the distribution of lithium but also its chemical state (chemical shift) with a resolution equivalent to EPMA (electron probe micro-analyzer). In this year, several materials related to liquid tritium breeding materials were analyzed using a soft X-ray spectrometer. These works were supported by ZE Research Program, IAE ZE31-C04.

2-1: Pb-Li intermetallic compound

Lead lithium intermetallic compound (such as PbLi_3) has not been well studied from the view point of tritium breeding material, unlike eutectic alloy of them ($\text{Pb}_{0.83}\text{Li}_{0.17}$, low melting point $\sim 508\text{K}$) which have been widely studied as a liquid tritium breeding material. The PbLi_3 compound can only be used as a solid breeding material due to the high melting point, but the several characteristics could be a breakthrough in fusion blanket development [1]. Since there are almost no previous researches on this intermetallic compound, synthesis and SXES analysis were performed in this fiscal year.

Fig. 1 shows an example of a cross section of an intermetallic compound (PbLi_3) prepared using an SUS316 steel capsule. Fig. 2 shows the SXES spectrum of the sample along with that of eutectic alloy ($\text{Pb}_{0.83}\text{Li}_{0.17}$). In the region of 0.050 to 0.055 keV where the characteristic peak of lithium is expected, the signal was weak and no clear difference has been observed so far. On the other hand, in the characteristic X-ray spectra of lead, there was a difference in the peak intensity ratios as shown in the

right of Fig. 2. It is well known that $\text{Pb}_{0.83}\text{Li}_{0.17}$ (eutectic composition) solidifies separating into the Pb_3Li intermetallic compound phase and the Pb phase dissolving Li, which might result in a peak intensity ratio different from that of the eutectic composition.

For the usage of this material as a tritium breeding material, it is necessary to confirm the change and gradient of the lithium concentration due to the release of lithium from the compound surface. The result showing the difference in the peak intensity ratios could be informative from this point of view.

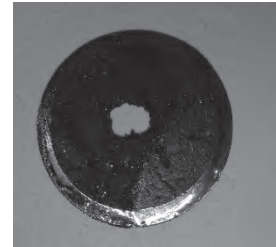


Fig.1: A sliced Pb-Li intermetallic compound prepared in an SUS tube.

2-2 Analysis of nitrogen in iron-titanium alloy

Lithium is also a promising tritium breeder like the $\text{Pb}_{0.83}\text{Li}_{0.17}$ eutectic alloy, but lithium easily absorbs nitrogen impurities, which are known to degrade the compatibility of lithium with materials. For the removal of nitrogen from lithium, a hot trap method using an Fe-Ti alloy has been studied and a direct quantifying method for nitrogen distribution in the alloy is required. Since the characteristic X-ray peaks of titanium and nitrogen are close to each other (both the K line of N and L line of Ti are around 0.39 keV), they cannot be quantified independently by ordinary EDX and WDX (energy and wavelength dispersive X-ray spectroscopies). The high energy resolution of SXES could enable individual quantification of N and Ti. Therefore, nitrogen analysis was performed on the cross section of the Fe-Ti alloy particles (Fe-5at% Ti, immersed in lithium containing 1000 wppm nitrogen at 550 °C for 81 hours for nitrogen absorption).

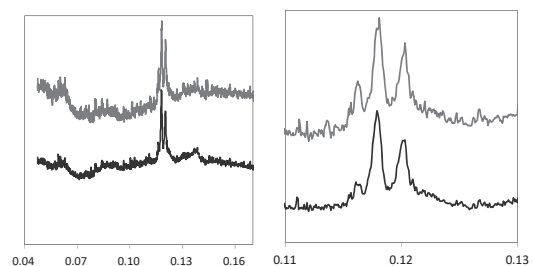


Fig.2: SXES spectra of PbLi compound and PbLi eutectic alloy (left: full range, right: characteristic X-ray of Pb, X-axis in keV, Upper: PbLi compound, Lower: PbLi eutectic alloy.)

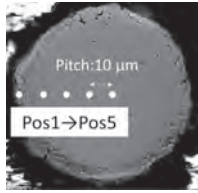


Fig.3: Analyzed points on the cross-section of Fe-Ti alloy pebble.

The analyzed positions in the cross section of the Fe-Ti alloy grain is shown in Fig. 3, and the characteristic X-ray spectra of nitrogen and titanium at each position are shown in Fig.4. Comparison with standard samples such as TiN and ZrN, it was found that the signal at 0.195 keV (the shoulder of the peak) is corresponding to nitrogen and the peak at about 0.197 keV is to titanium. It was confirmed that nitrogen had penetrated into the inside of the alloy, and SXES is shown to be effective also for this analysis

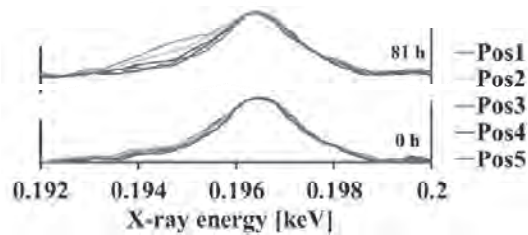


Fig.4: Soft X-ray count in each point. The counts around 0.195 keV corresponding to N increase when the alloy was immersed in N-containing Li.

3. Starting up of 3-D calculation of blanket performances

Three-dimensional calculations for self-cooled liquid blanket systems have been started from thermo-fluid analyses using the STREAM code, since the heat removal performance will decide the basic configuration of the systems. The temperature and flow velocity distribution are also key parameters to discuss behaviors of hydrogen fuels, corrosion behaviors, etc. in the blanket system.

For the analyses, magnetic field and nuclear heating distributions in a helical reactor were analyzed and equations to input the distributions into the STREAM code were obtained by curve fittings. Figs. 5 (a)-(c) show schematic drawing of the blanket in the helical reactor FFHR-d1 design [2], distributions of nuclear heating in the radial direction

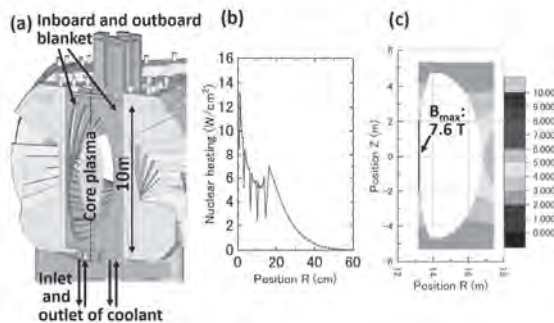


Fig.5: (a) Blanket of helical reactor FFHR-d1, (b) distribution of nuclear reaction, (c) distribution of magnetic fields.

and strength of magnetic field in the blanket region. In the FFHR-d1 design, the height of the blanket is ~10 m and the coolant flows through the vertical coolant channels perpendicular to the magnetic field. In addition to the nuclear heating, the heat load of 0.1-0.2 MW/m² from the core plasma is applied to the surface of the blanket. Fig. 6 (a) shows the simplified calculation model to simulate the cooling performance of a Pb_{0.83}Li_{0.17} coolant in the blanket.

The calculated temperature distribution in the Pb-Li coolant channels is shown in Fig. 6 (b). If the metal coolant channel is not electrically insulated, the MHD pressure drop in the Pb-Li coolant is calculated to be ~110 MPa under the strong magnetic field and the circulation of the coolant will be impossible. The electrical insulating coating on the metal coolant channels will reduce the pressure drop to ~0.4 MPa and enable the efficient circulation. The temperature of the first wall (the surface facing to the core plasma) is ~490 °C for the heat load of 0.1 MW/m² and it is lower than the maximum allowable temperature of a low activation ferritic steel, i.e. 550 °C. The maximum temperature of the blanket surface is dominated almost by the heat load from the core plasma and the temperature increases to ~590 °C for the heat load of 0.2 MW/m². To suppress the maximum temperature in the blanket, horizontal coolant channel configurations where the coolant flows in parallel with the magnetic field (Fig. 7) are being investigated.

In the future calculations, results obtained in various experimental studies on blanket technologies such as hydrogen fuel and corrosion behaviors will be joined to the three-dimensional calculations for the integrated blanket design studies.

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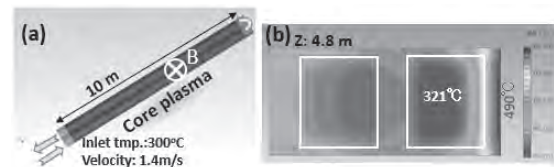


Fig.6: (a) Calculation model of blanket for helical reactor (b) Temperature distribution in horizontal cross section.

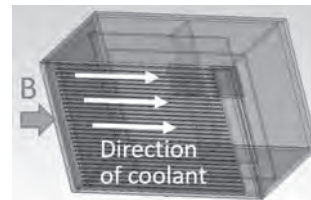


Fig.7: Example of calculation model with horizontal coolant channels under investigation.

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Chemical Reaction Complex Processes Research Section

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 T. Kodaki, Associate Professor
 T. Ymamoto, Assistant Professor

1. Introduction

In this research section, we study on electrochemistry, materials science, genetic engineering and protein engineering. We also apply them to the developments of efficient metal plating processes, new secondary batteries and efficient bioethanol production processes.

In this fiscal year, we have researched an electrodeposition processes of titanium and tungsten, a potassium secondary battery using ionic liquids, and an efficient bioethanol production process using ionic liquids.

2. Development of New Plating Processes of Titanium and Tungsten Using Molten Salt Electrolytes

It is well known that refractory metals [1,2] and Si [3] can be electrodeposited from fluoride-based molten salts like LiF-KF and LiF-NaF-KF. One of the problems in the previous studies employing fluoride-based molten salts was the difficulty in removing the salt adhered to the deposits, because the solubility of LiF and NaF in water is very low. From this background, we have proposed a new electrodeposition process of Si [4] and Ti [5,6] using eutectic KF-KCl (45:55 mol%, m.p. 878 K) melts. Since both KF and KCl are highly soluble in water, the adhered salt can be removed easily by washing with water. Recently, we found that eutectic CsF-CsCl (50:50 mol%) melts are also promising due to the lower melting point (712 K) and the high solubility in water. In the present study, we investigated the electrodeposition of Si, Ti and W in molten KF-KCl or CsF-CsCl.

Electrodeposition of Ti was conducted in molten KF-KCl at 923 K to which K_2TiF_6 (2.0 mol%) and Ti (1.3 mol%) were added. In this molten salt, a comproportionation reaction proceeds to form Ti(III) ions from Ti(IV) ions and Ti(0). Fig. 1 shows surface and cross-sectional SEM images of the sample prepared by galvanostatic electrolysis at 100 mA cm^{-2} for 25 min. A dense and smooth Ti film was successfully obtained on a Ni substrate. An electrochemical corrosion resistance test in simulated seawater proved that the film has a good property similar with Ti plate.

Electrodeposition of W was also achieved in KF-KCl- WO_3 (2.0 mol% added) at 923 K. When CsF-CsCl- WO_3 (2.0 mol% added) was used at lower temp. of 873 K, a more smooth W film was obtained as shown in Fig. 2.

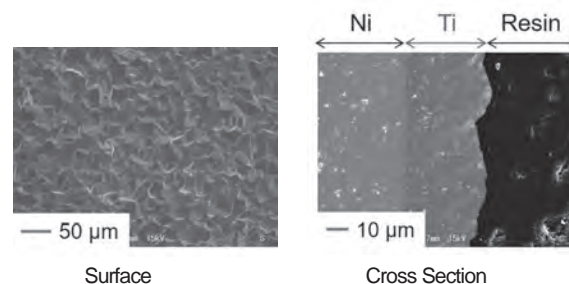


Fig. 1. SEM images of the Ti film obtained on a Ni plate at 100 mA cm^{-2} for 25 min in molten KF-KCl (KF:KCl=45:55 mol%) at 923 K after the addition of K_2TiF_6 (2.0 mol%) and Ti (1.3 mol%).

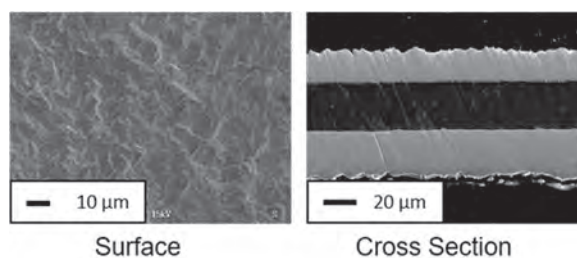


Fig. 2. SEM images of the W film obtained on a Cu plate at 12.5 mA cm^{-2} for 120 min in molten CsF-CsCl (CsF:CsCl=50:50 mol%) at 873 K after the addition of WO_3 (2.0 mol%).

3. Development of Potassium Secondary Batteries Using Ionic Liquid Electrolytes

The development of large-scaled electrical energy storage (EES) devices are essential to establish low-carbon society using renewable energy resources such as solar and wind power because the electric power generation of these resources are largely dependent on weather. Although current lithium-ion batteries are candidates for large-scaled EES devices, scarce lithium resources and flammable organic solvents are used as main components, which might be a major barrier to the further distribution.

Our group has focused on potassium secondary batteries using ionic liquid electrolytes because potassium resources are abundant in the Earth's crust and ionic liquids possess high safety such as negligible volatility and

non-flammability. We have previously reported the physicochemical properties of a novel potassium-based electrolyte, K[FSA]-[C₃C₁pyrr][FSA] (C₃C₁pyrr = *N*-methyl-*N*-propylpyrrolidinium) [7].

Then, we investigated charge-discharge behavior of tin-based negative electrodes. Fig. 3 shows the discharge capacities of the tin negative electrode for 100 charge-discharge cycles. Initial discharge capacity was 186 mAh (g-Sn)⁻¹, which was 82% of the theoretical capacity (226 mAh (g-Sn)⁻¹ for KSn phase formation). Even after 100 cycles, the discharge capacity of 173 mAh (g-Sn)⁻¹ was maintained, corresponding to the high capacity retention ratio of 93%. The charge-discharge performance obtained in this study is superior to the previous studies using organic solvent-based electrolytes. Thus, the combination of the ionic liquid electrolyte and the tin negative electrode is promising for safe and high-performance potassium secondary batteries.

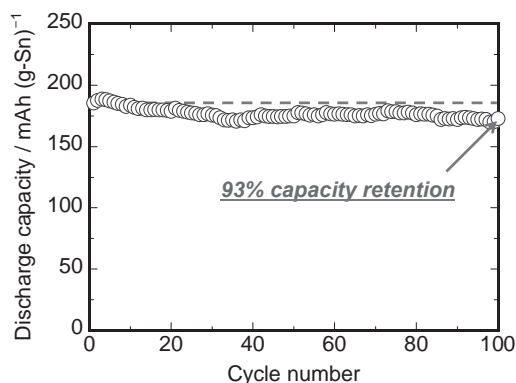


Fig. 3. Discharge capacities of the tin negative electrode for 100 cycles at 298 K. Electrolyte: K[FSA]-[C₃C₁pyrr][FSA] (molar fraction: $x(\text{K[FSA]}) = 0.20$). Current density: 20 mA (g-Sn)⁻¹.

4. Efficient Bioethanol Production from Cellulose Using Ionic Liquid

Cellulose is the most abundant natural compound among woody biomass and expected to be a source for biofuel such as bioethanol. However, rigid crystal structure of cellulose makes it difficult to hydrolyze to glucose. Recently, pretreatment with ionic liquids was found to be effective for hydrolysis of cellulose by cellulase.

In this fiscal year, a yeast strain with increased tolerance to ionic liquid was developed in order to improve fermentation efficiency in the presence of ionic liquid. An ionic liquid tolerant yeast strain was isolated by culturing repeatedly in the medium with increased concentrations of ionic liquid, 1-butyl-3-methylimidazolium chloride ([Bmim]Cl). This yeast strain can grow in the presence of 500 mM [Bmim]Cl (Fig. 4) and also fermented ethanol efficiently (Fig. 5).

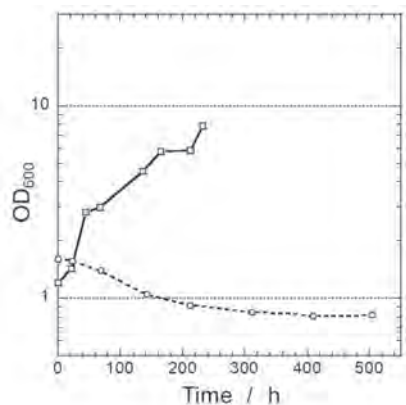


Fig. 4. Growth in the presence of 500 mM [Bmim]Cl. ionic liquid tolerant strain: solid line, wild type strain: dashed line.

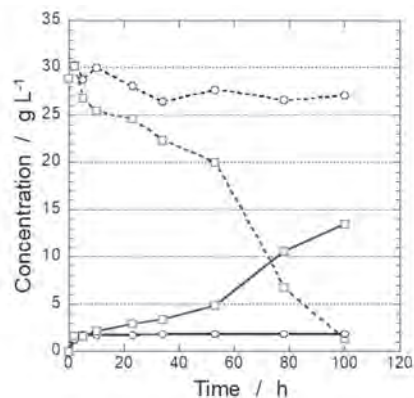


Fig. 5. Ethanol fermentation in the presence of 500 mM [Bmim]Cl. ionic liquid tolerant strain: square, wild type strain: circle, ethanol: solid line, glucose: dashed line.

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Molecular Nanotechnology Research Section

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S. Nobusue, Assistant Professor

1. Introduction

Nanotechnology is essential for highly efficient energy use. Our group studies the basics of assembling small molecules into the advanced materials and devices in energy sector with high efficiency. We have already developed several unique techniques which are totally new molecular assembling methodology such as 'electro-chemical Epitaxial Polymerization' and 'Two-Zone Chemical Vapor Deposition (2Z-CVD)' which enable to produce molecular wires on metal surface from small molecules. By using these techniques, organic electronic devices such as field-effect transistors and organic solar cells will be developed.

Main research achievements in Molecular Nanotechnology Research Section in 2019 are described below.

2. Bottom-Up On-Surface Synthesis of Two-Dimensional Graphene Nanoribbon Networks and Their Thermoelectric Properties

Graphene nanoribbons (GNRs) have shown great potential for electronics, optoelectronics, and photonics. These properties strongly depend on width and edge structure of them. Therefore, precisely controlled width and edge structure are required for desired properties. Bottom-up synthesis of GNRs is a one of suitable method to satisfy these requirements because of definition of their edge structures and widths by the shape of precursors. Atomically precise synthesis of armchair-edged GNRs have already been achieved under ultra-high vacuum (UHV) condition. However, given GNRs in this method were low yield and density was still low. Therefore, it was difficult to develop organic electronic devices with them. To develop devices, high-yield fabrication of assembled GNR films, isolation, and device fabrication are required.

We have developed 2Z-CVD to produce densely packed, parallelly aligned self-assembled GNRs on Au(111) under low vacuum condition from halogenated polycyclic aromatic hydrocarbon (PAH) precursors. This technique successfully produced a series of armchair-edged GNRs in high yield. Attractive features of this method originate from an independent

temperature-control of radical-generation process (zone 1) and the growth process (zone 2), which afforded GNRs in high yield without using UHV conditions. The precursor was sublimated to the Au(111) substrate in zone 2 by passing through zone 1 in a quartz tube. The mechanism is supposed to involve radical generation in zone 1, polymerization of the radicals on the Au(111) substrate in zone 2, and subsequent dehydrogenation to form GNRs.¹ Additionally, we demonstrate a new concept of 'conformation-controlled surface catalysis'; the 2Z-CVD of the 'Z-bar-linkage' precursor, which represents two terphenyl units are linked like a 'Z', exhibiting flexible geometry that allows it to adopt chiral conformations with height-asymmetry on a Au(111) surface, results in the efficient formation of acene-type GNRs with a width of 1.45 nm through optimized cascade reactions. These cascade reactions on surface include the production of self-assembled homochiral polymers in a chain with a planar conformation, followed by efficient stepwise dehydrogenation via a conformation-controlled mechanism. Our proposed concept analogous to the biological catalyst, enzyme, is useful for the fabrication of new nanocarbon materials.²

On the other hand, fully π -conjugated 2D structure attract much attention since they can provide conducting carbon-based nanostructures with holey structure suitable for various electronic applications. Utilization of large fully π -conjugated building blocks such as GNRs, which are 1D carbon-based nanowires, is becoming a promising approach to produce extended 2D π -conjugated systems via surface assisted lateral fusion of GNR chains. However, it was difficult to efficiently create such sophisticated GNR-linkage structures, since their formation is based on a stochastic surface reaction that requires closed proximity between the precursors on the surface.

We have already successfully produced well-organized acene-type GNRs. They were used for producing carbon-based 2D materials, named 2D-Graphene Nanoribbon Networks (GNNs) because this is considered to be suitable for providing 2D structures via lateral fusion of GNRs.

we have fabricated acene- and armchair-type

2D-GNNs on the surface of Au(111) through the thermally induced interchain reactions of densely packed self-assembled GNRs (5-CGNR-1-1 and 7-AGNR), using the new concept of transforming 1D chains into a 2D network. The 5-CGNR-1-1 and 7-AGNR on Au(111) were produced by 2Z-CVD using the precursor of DBQP and DBSP, respectively. The STM images clearly confirm the generation of 2D-GNNs on the surface of Au(111). The structure of 2D-GNNs consist of hybridized junctions of GNRs with various widths, showing both metallic-like and semiconducting characteristics. Particularly, around fourfold increase in the electrical conductivity of 2D-GNNs when compared to the corresponding GNRs, also confirms the formation of a 2D network structure. The thermal conductivity of 2D-GNNs generated from 5-CGNR-1-1 shows a value of $0.11 \text{ Wm}^{-1}\text{K}^{-1}$, which is one of the lowest values among carbon-based materials as well as inorganic semiconductor materials, while maintaining the electrical conductivity of 188 Sm^{-1} . These findings will open new perspectives in the field of research on the utilization of GNRs for TE applications.³

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Biofunctional Chemistry Research Section

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1. Introduction

A transition to renewable energy technologies requires new chemistry to learn from nature. Nature has found fantastic solutions to convert solar energy to produce chemicals and to utilize them in the exceptionally efficient manners for almost 3 billion years. It is our challenge to understand the efficient bioenergetic processes of nature and to construct bio-inspired energy utilization systems. The research interests in our group focus on the design of biomacromolecules and their assemblies for molecular recognition, catalysis and signal transduction in water, the solvent of life. We take synthetic, organic chemical, biochemical and biophysical approaches to understand the biological molecular recognition and chemical reactions. Proteins and protein/nucleic acids assemblies are explored to realize biomimetic function of biological systems, such as visualization of cellular signals by fluorescent biosensors, directed self-assembly of peptides and proteins to build up nanobiomaterials, tailoring artificial receptors and enzymes based on the complex of RNA and a peptide or a protein, and reconstitution of the functional assemblies of receptors and enzymes on the nanoarchitectures. Followings are main research achievements in fiscal year 2019.

2. Rational design of a DNA sequence-specific modular protein tag by tuning the alkylation kinetics

Sequence-selective chemical modification of DNA by synthetic ligands has been a long-standing challenge in the field of chemistry. Even when the ligand consists of a sequence-specific DNA binding domain and reactive group, sequence-selective reactions by these ligands are often accompanied by off-target reactions. A basic principle to design DNA modifiers that react at specific sites exclusively governed by DNA sequence recognition remains to be established. We have previously reported selective DNA modification by a self-ligating protein tag conjugated with a DNA-binding domain, termed as a modular adaptor, and orthogonal application of modular adaptors by relying on the chemoselectivity of the protein tag. The sequence-specific crosslinking

reaction by the modular adaptor is thought to proceed in two steps (Fig. 1): the first step involves the formation of a DNA–protein complex, while in the second step, a proximity-driven intermolecular cross-linking occurs. According to this scheme, the specific crosslinking reaction of a modular adaptor would be driven by the DNA recognition process only when the dissociation rate of the DNA complex is much higher than the rate constant for the alkylation reaction. In this study, as a proof of principle, a set of combinations for modular adaptors and their substrates were utilized to evaluate the reactions. Three types of modular adaptors consisting of a single type of self-ligating tag and three types of DNA binding proteins fulfill the kinetic requirements for the reaction of the self-ligating tag with a substrate and the dissociation of the DNA–protein complex. These modular adaptors actually undergo sequence-specific crosslinking reactions exclusively driven by the recognition of a specific DNA sequence. The design principle of sequence-specific modular adaptors based on the kinetic aspects of complex formation and chemical modification is applicable for developing recognition-driven selective modifiers for proteins and other biological macromolecules.

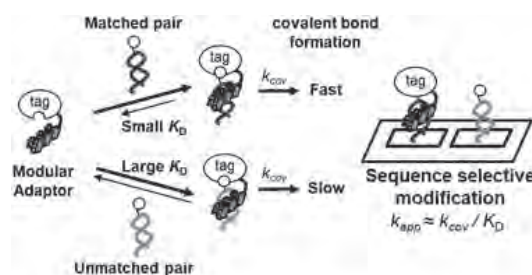


Fig. 1 Schematic illustrations of intrusion of the sequence selective modular protein tag. Orthogonal cross-linking reactions driven by the sequence selectivity of DNA-binding domains and chemo-selective cross-linking reactions by the protein tag.

3. Reaction of ribulose biphosphate carboxylase/oxygenase assembled on a DNA scaffold

Ribulose-1,5-biphosphate carboxylase/oxygenase (RuBisCO), an enzyme in the Calvin-Benson-Bassham cycle of photosynthesis, catalyzes the first step of CO₂ fixation in plants, algae, and photosynthetic bacteria. Despite of the important function in the global carbon cycle, RuBisCO suffers from a slow reaction rate and a competing reaction with O₂ which draw attentions to improve the enzyme efficiency. In this study, a RuBisCO dimer from *Rhodospirillum rubrum* was assembled on a DNA scaffold using a dimeric DNA binding protein as an adaptor. The enzyme assembly was characterized by atomic force microscopy and RuBisCO assembled on the DNA scaffold showed avid enzymatic activity with retaining its parent carboxylase function. To mimic the environment of the natural microcompartment in cyanobacterial carboxysome that encapsulate the second enzyme carbonic anhydrase (CA) with RuBisCO, RuBisCO was next co-assembled with CA on the DNA scaffold (Fig. 2). Although the natural carboxysome assembly is believed to enhance the RuBisCO activity, the co-assembly of RuBisCO and CA reduced the RuBisCO activity, suggesting that the preferential CO₂ dehydration by CA reduced the RuBisCO reaction rate. In line with the recent study, our results suggest that the proximity in the interenzyme distance of RuBisCO and CA is not the crucial determinant for the enhanced RuBisCO activity in carboxysome. The assembly of RuBisCO and CA on DNA scaffold provides a platform for further study on the spatial control of RuBisCO and associating enzymes.

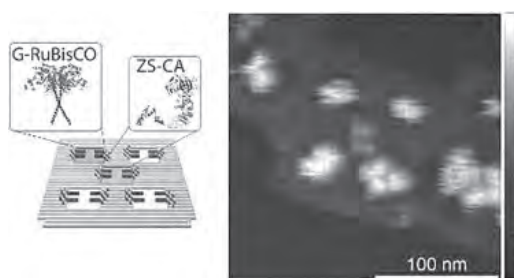


Fig. 2 Assembling G-RuBisCO and ZS-CA on the DNA scaffold. G-RuBisCO and ZS-CA were assembled on the DNA origami containing the binding sites for ZS adaptor (for ZS-CA) at the center cavity and for GCN4 adaptor (for G-RuBisCO) at the other cavities. An illustration of DNA scaffold with the models of G-RuBisCO and ZS-CA is shown in the left and AFM image in the right.

4. Fluorescence detection of the nitric oxide-induced structural change at the putative nitric oxide sensing segment of TRPC5

The plausible nitric oxide (NO)-sensing module of TRPC5 was incorporated in a enhanced green fluorescent protein (EGFP) to evaluate its conformational change as an optical response upon the reaction with NO. Two cysteine residues located in the NO-sensing module have been proposed to form a disulfide bond through S-nitrosylation of the thiol group by NO. Modification of the cysteine residues by NO resulted a ratiometric change of EGFP emission through transducing the conformational change of NO-sensing module to the EGFP chromophore (Fig. 3). The oxidized form of NO-sensing module fused EGFP changed the intensity of emission spectra upon reduction of the disulfide bond at the NO-reactive module. The NO-sensing module fused EGFP in its reduced form avidly reacted with NO and realized the ratiometric fluorescence intensity changes depending on the formation of disulfide bond. These results support the notion that NO induces a conformational change at the putative NO-sensing segment of TRPC5, and provide a prototype for the genetically encoded cellular NO sensors.

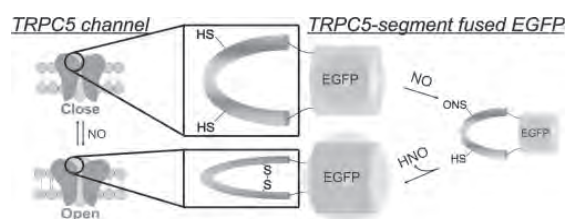


Fig. 3 Schematic illustrations of EGFP-TRPC5. Two cysteine residues located in the NO-sensing module have been proposed to form a disulfide bond through S-nitrosylation of the thiol group by NO. Modification of the cysteine residues by NO resulted a ratiometric change of EGFP emission through transducing the conformational change of NO-sensing module to the EGFP chromophore.

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Collaboration Works

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森井孝, Seoul National University (大韓民国), 特定空間に配置された酵素複合体の構築

森井孝, 中田栄司, Rajendran Arivazhagan, Ewha Womans University (大韓民国), 小分子による酵素機構の解明

森井孝, 仲野瞬, POSTECH (大韓民国), 蛍光性バイオセンサーの構築

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Structural Energy Bioscience Research Section

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 T. Nagata, Associate Professor
 T. Mashima, Assistant Professor

1. Introduction

We explore the way how biomolecules such as proteins (involving enzymes) and functional nucleic acids (DNA and RNA) work at atomic resolution based on structural biology with NMR. We determine both static and dynamical structures with the aid of our own development of the new methodology and elucidate the underlying mechanism of functions of these biomolecules. Structural biological approach is also applied to analyze enzymes involved in degradation of wood biomass at atomic resolution. The analysis is useful to develop the way to extract energy and valuable materials that can be used as starting materials of various products from the wood biomass. Thus, we pursue to contribute to the paradigm shift from oil refinery to biorefinery. Followings are main research achievements in the year of 2019.

2. Development and structural determination of anti-prion aptamers that block pathological conformational conversion of prion protein

Prion diseases are fatal neurodegenerative disorders including Creutzfeldt–Jakob disease in humans and bovine spongiform encephalopathy in cattle. The conformational transition of prion protein (PrP) from a normal form (PrP^C) into an abnormal form (PrP^{Sc}) is a key event in the pathogenesis of prion diseases. We rationally designed new potent anti-prion RNA aptamers, r(GGAGGAGGAGGAGGAGGAGGAGGA) (R24) and r(GGAGGAGGAGGAGGAGGAGGA-A-GGAGGAGGAGGA) (R12-A-R12) and proved their high anti-prion abilities to block the pathological conformational conversion of PrP by means of a cell-based assay (in collaboration with Profs. Kuwata and Kamatari). We also determined the structure of R12-A-R12 by NMR. It was revealed clearly that a single R12-A-R12 molecule forms a unique quadruplex structure. Then, a model of R12-A-R12 in a complex with a prion protein was constructed. The model indicated that R12-A-R12 can simultaneously interact with two portions (P1 and P16) of the prion protein (Figure 1). This binding mode can rationalize the high affinity of the aptamer toward the prion protein and resultant high anti-prion activity. Alzheimer's disease (AD) is one of the most common neurodegenerative disorders and the link

between amyloid β (A β) and AD has been suggested. It was reported that prion protein acts as a receptor of the A β oligomer for the transmission of pathological signal into cells. The aptamers can bind very strongly to the prion protein, which could interfere with the receptor function of prion protein. Therefore, R24 and R12-A-R12 may have the therapeutic potential for treating not only prion disease but also AD.

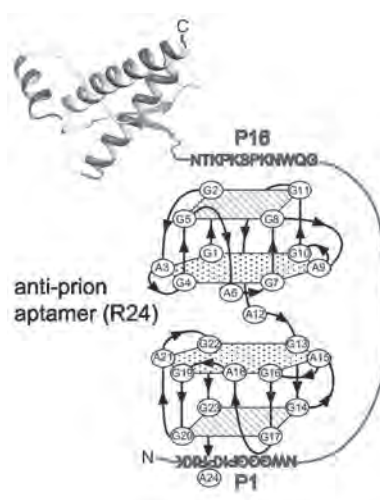


Figure 1. Binding mode of a highly potent anti-prion aptamer, R24, with a prion protein, as determined by NMR.

3. Analysis of the conformational change of FUS upon binding of telomere-related DNA/RNA

Fused in sarcoma (FUS) is an RNA/DNA-binding protein that triggers a repression of the transcription of the cyclin D1 (CCND1) gene when the genome is damaged. The C-terminal half of FUS is responsible for binding with a long non-coding RNA, named pncRNA. This binding hypothetically causes the conformational change of FUS to let its N-terminal half to bind to transcription coactivators CBP/p300, resulting in repression of the CCND1 gene transcription. Our previous fluorescence resonance energy transfer (FRET) analyses indicated that FUS indeed exhibits conformational change upon binding with pncRNA. Here, we newly demonstrated using FRET that the conformational change of FUS is also caused by another targets, telomeric DNA and

telomeric repeat-containing RNA. Additionally, we applied high-speed atomic force microscopy (HS-AFM) and attempted to visualize the conformational change of FUS. Our data indicated that FUS forms a compact structure by itself. However, on binding of pncRNA, FUS changed its conformation extensively as it had been indicated by FRET analyses. We are currently characterizing the structural features of the FUS:pncRNA complex to obtain a mechanistic insight into transcriptional repression by FUS and pncRNA.

4. Activity analysis of fungal glucuronoyl esterase linked with carbohydrate-binding module

Woody biomass is the most abundant renewable feedstock on earth, which is applicable to the production of energy and valuable materials. The components of woody biomass, cellulose, hemicellulose, and lignin, are rigidly associated together to form the lignin-carbohydrate complex (LCC). Association of hemicellulose and lignin in LCC is strengthened by covalent bonds named lignin-carbohydrate (LC) linkages. Fungal glucuronoyl esterases (FGEs) catalyze the cleavage of ester-type LC linkage. We previously characterized two FGEs, and demonstrated that the catalytic domain of FGE of *Pleurotus eryngii* (*PeGE*) has the highest activity among the reported FGEs. This year, we established the *Pichia pastoris* expression system for the full-length *PeGE* (FL-*PeGE*), where the carbohydrate-binding module (CBM) is linked with the catalytic domain. We supposed that CBM may enhance the substrate affinity of *PeGE* by binding to the polysaccharide moiety of woody biomass, by which the activity may be enforced. Unexpectedly, FL-*PeGE* exhibited comparable activity with the catalytic domain of *PeGE* alone. LCC fraction that is rich in the ester-type LC linkage was extracted from woody biomass. Cleavage of LC linkage by FL-*PeGE* is currently under investigation by NMR spectroscopy.

5. Synergistic effect of lytic polysaccharide monoxygenase on cellulase cocktail activity

Cellulose-active lytic polysaccharide monoxygenases (LPMOs) is an enzyme that is involved in the degradation of recalcitrant crystalline cellulose in woody biomass. LPMOs catalyze the oxidative cleavage of glycosidic linkage on the surface of crystalline cellulose and decreases the crystallinity of the cellulose, which accelerates the degradation of cellulose by hydrolytic cellulases. We previously developed a high-yield *Pichia pastoris* expression system of LPMO. Here, the activity of LPMO was confirmed by the oxidation of dimethoxy phenol (DMP). Subsequently, the effect of LPMO to the cellulose degradation by hydrolytic cellulases

was investigated. LPMO exhibited a synergistic effect on the cellulase cocktail activity, by which the glucose yield from microcrystalline cellulose increased by > 30% (Figure 2).

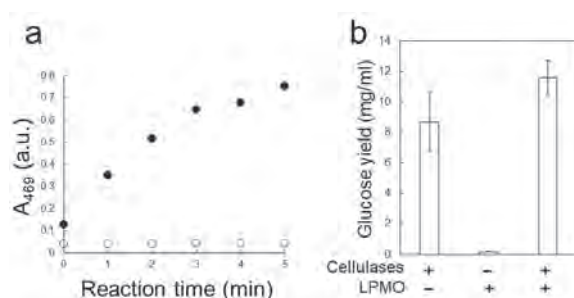


Figure 2. (a) The activity assay of LPMO. DMP was incubated in the presence (closed circle) and absence (open circle) of LPMO. The oxidized product formation was monitored by the absorbance at 469 nm. (b) Synergistic effect of cellulases and LPMO. LPMO itself did not produce glucose from microcrystalline cellulose. Whereas, the glucose yield by cellulases increased by the addition of LPMO.

6. The structural stability of nucleic acids in living human cells studied by in-cell NMR

The properties of nucleic acids such as structure, stability, and dynamics in cells could be different from those in dilute *in vitro* condition. In-cell NMR is a prominent method for measuring those properties in living cells. Previously, we reported the first in-cell NMR spectra of nucleic acids in living human cells, where the nucleic acids of interest were introduced into living human cells by using the pore-forming toxic protein, streptolysin O, and resealing technique. This time, we installed the bioreactor system, which can supply fresh culture medium to the NMR tube containing the cells having the nucleic acid of interest. This bioreactor system extended the lifetime of the cells, and thereby the NMR signals of the nucleic acids inside the cells have been observed even after 24 hours. The extension of the measurable time of in-cell NMR enabled us to evaluate the structural stability of the hairpin structure formed by 2'-O-methylated RNA in living cells. The hydrogen-bonded imino protons of the base pairs exchange with the protons of bulk water only when the base pairings are disrupted. Therefore, the exchange rates of the imino protons can be used as probes to evaluate the stabilities of the base pairs. Recently, the exchange rate of the imino proton of nucleic acid in living cells was successfully measured for the first time. This gave the insight on the stability of base pairs in cells.

Collaboration Works

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近藤敬子, 若手研究, テロメアの伸長抑制に関わる TLS 蛋白質による四重鎖核酸認識の構造基盤解明

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2. Others

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片平正人, 新エネルギー・産業技術総合開発機構,

NEDO 先導研究プログラム/新産業創出新技術先導研究プログラム/分子触媒システムによる木質バイオマス変換プロセスの研究開発

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Advanced Energy Utilization Division

A. Rajendran, Junior Associate Professor

1. Introduction

Catenanes and rotaxanes are multicomponent structures of topologically-interlocked molecules. The catenanes are prepared by interlocking two chains of macromolecules, whereas the rotaxanes contain a linear axle with a bulky stoppers at each end in which a ring-like structure is interlocked.^[1] These interlocked structures have been realized long time ago in macromolecular chemistry^[2] and preparation of these structures by using DNA or DNA nanostructures are of ongoing interest. These assemblies have potential applications in molecular motors, logical devices, sensors, and so on. Here, I aimed to prepare the DNA catenane- and DNA rotaxane-like structures inside a frame shaped DNA origami (scaffolded DNA origami – a method to self-assemble DNA into the arbitrary two- and three-dimensional structures as templates)^[3] and use these assemblies as substrates for both restriction enzymes and topoisomerases (Topos). Further, these structures will be used for the screening of Topo inhibitors.

The DNA Topos have been identified as the potential targets of a variety of therapeutics including anticancer drugs. The DNA topology such as overwinding or underwinding that arises due to the intertwined nature of the DNA double helices are regulated by the Topo enzymes.^[4] If the DNA overwinding problem that arises during the replication and transcription is not relaxed, it ultimately inhibits the functions of the enzymes involved in these processes. Topos control the topological conditions by transiently cleaving the phosphodiester bond, which

generates a Topo-DNA cleavage complex. Once the winding stress is resolved, the enzyme-mediated DNA break is resealed. This process is critical for the healthy cells to survive and function normally, and failure to resealed the DNA break can ultimately lead to cell death. Topos involve in step-by-step processes such as binding of Topo to DNA, ATP driven strand passage, strand cleavage by Topo, formation of Topo-DNA cleavage complex, religation of cleaved DNA, and catalytic cycle after DNA cleavage (Figure 1). All these steps are of great interest as potential targets for the development of anticancer drugs.^[5] Despite the development of various Topo-inhibitors, the progress towards understanding how these inhibitors interact with these enzymes is impeded by the drawbacks in the traditional methods. For instance, it is not well understood at which step of the enzyme reaction is inhibited by a particular drug. Thus, to understand the Topos reaction and the mechanisms of the inhibitors, it is necessary to develop a versatile method.

2. Preparation of topologically-interlocked DNA structures inside a DNA origami frame

Since the Topo enzymes target the topologically-constrained DNAs, the interlocked DNA structures such as catenane and rotaxane can be used as the substrates to investigate the Topos functions and their inhibitors.^[6] The fabrication of the duplex DNA catenanes and rotaxanes inside the relatively larger and complex DNA nanostructures such as DNA origami has not yet been realized. I have been collaborating with the research groups of Prof.

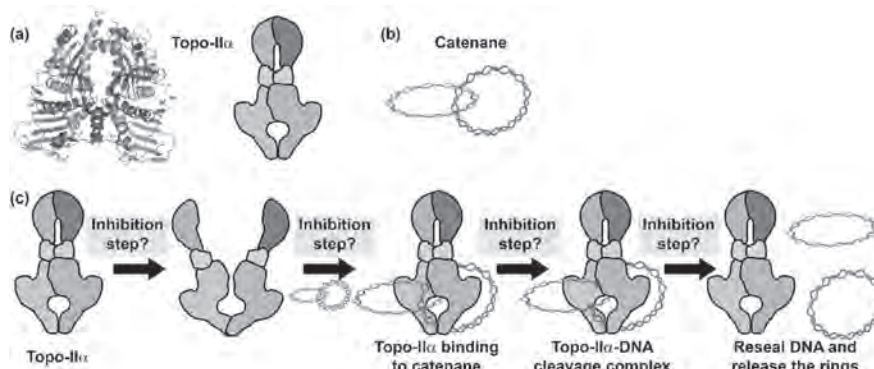


Figure 1. (a) The crystal structure (left, PDB: 1zxm) and graphical illustration (right) of the topoisomerase II α (Topo-II α). (b) The topologically interlocked DNA catenane. (c) The mechanism of Topo-II α to release the interlocked DNAs in the catenane. The possible inhibition steps by various drug molecules are indicated.

Takashi Morii at IAE, Kyoto University and Prof. Youngjoo Kwon at Ewha Womans University, South Korea for the preparation of the interlocked supramolecular assemblies inside a DNA origami.

At first, we have constructed the topologically-interlocked DNA catenane- and rotaxane-like structures inside a DNA origami frame. The formation of the DNA origami frame^[7-8] and the insertion of the catenane- and rotaxane-like structures were successfully characterized by agarose gel electrophoresis and high-speed atomic force microscopy (HS-AFM).^[9-13] We could successfully fabricate the rotaxane- and catenane-like structures with the average yield of 30 and 60%, respectively. To increase the stability of these functional structures, the nicks in these structures were sealed by using T4 DNA ligase. The ligation was also confirmed by the thermal treatment of these structures, where the ligated samples were stable at high temperature treatment while the unligated samples failed to keep the folded structures. The experimental conditions such as the amount of salt, annealing temperatures, concentration of the DNA strands were optimized. The purification and quantification methods to get rid of the excessive staples and unbound catenane/rotaxane rings were also established. Further, we have investigated the stability of the DNA origami frame and the catenane/rotaxane ring structures in the presence of various kinds of Topo inhibitors. Both the origami and the DNA ring were stable against the Topo inhibitors for several hours at room temperature. This indicated that the DNA origami based analysis of Topo inhibitors could be successfully carried out.

3. Enzymatic reactions on the DNA catenane- and rotaxane-like structures

After successful preparation of the interlocked structures, we have performed the enzymatic reactions on them. The restriction enzyme PstI has the scission site in the linear duplex of the rotaxane-like structure and catenane ring, and XbaI cuts the ring of both rotaxane- and catenane-like structures. After the restriction enzyme treatment, the structures were analyzed by both agarose gel electrophoresis and AFM imaging. After the overnight incubation, the yield of the reactions were estimated to be 50% (PstI for rotaxane), 46% (XbaI for rotaxane), 45% (PstI for catenane) and 54% (XbaI for catenane), indicating the success of the reaction.

Further, we have investigated the TopoII α reaction on these interlocked functional structures and found that about 16 and 10% reactions respectively on the catenane- and rotaxane-like structures. We are now working on the screening of Topo inhibitors. Such a

screening will be carried out by the direct and real-time characterization methods such as HS-AFM and fluorescence imaging. Apart from the Topo reactions and inhibitor screening, the fabrication of the topologically interlocked structures within a DNA origami nanostructure is also promising in the fields of molecular switches, motors, sensors, and logic devices.^[1] Topologically interesting structures such as Borromean rings, catenanes, and knots have already been prepared by using DNA.^[1] Also, the complexity of the catenane^[14] and rotaxane^[15] structures were increased by constructing them by the DNA origami method. However, for the first time we have fabricated the duplex DNA catenanes and rotaxanes inside the relatively larger and complex DNA nanostructures such as DNA origami and applied for the enzymatic reactions and drug analysis.

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Presentations

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Self-Assembly Science Research Section

M. Kinoshita, Professor

A variety of self-assembly and ordering processes in biological systems, which occur at molecular levels, are sustaining life. Biopolymers, a diversity of molecular and ionic species, or water is simply *material* when each of them is separately present. However, the complicated correlations among these material constituents can lead to *life*. We are elucidating these correlations, uncovering the mechanism of the biological processes, and clarifying the roles of water by developing special theories based on statistical mechanics and hydration thermodynamics. The current subjects are hydrophobic and hydrophilic hydrations, entropic force, behavior of confined liquids, folding/unfolding mechanisms of proteins, molecular recognition, enhancement of the thermal stability of membrane proteins by amino-acid mutations, and functioning of ATP-driven proteins.

(1) An accurate and rapid method for calculating hydration free energies of a variety of solutes including proteins [1]

A new method is developed for calculating hydration free energies (HFEs) of polyatomic solutes. The solute insertion is decomposed into the creation of a cavity in water matching the geometric characteristics of the solute at the atomic level (process 1) and the incorporation of solute-water van der Waals and electrostatic interactions (process 2). The angle-dependent integral equation theory combined with our morphometric approach and the three-dimensional (3D) interaction site model theory are applied to processes 1 and 2, respectively. Neither a stage of training nor parameterization is necessitated. For solutes with various sizes including proteins, the HFEs calculated by the new method are compared to those obtained using a molecular dynamics simulation based on solution theory in energy representation), currently the most reliable tool. The agreement is very good especially for proteins. The new method is characterized by the following: The calculation can rapidly be finished; a solute possessing a significantly large total charge can be handled without difficulty; and since it yields not only the HFE but also its many physically insightful, energetic and entropic components, it is best suited to the elucidation of mechanisms of diverse phenomena such as the receptor-ligand binding, different types of molecular recognition, and protein folding, denaturation, and association.

(2) Mechanism of globule-to-coil transition of poly(*N*-isopropylacrylamide) (PNIPAM) in water: Relevance to cold denaturation of a protein [2]

In water, PNIPAM is in a soluble coil state below the lower critical soluble temperature (LCST) but in

an insoluble globule state above LCST. As the temperature decreases, PNIPAM exhibits a globule-to-coil transition at LCST~305 K. We generate structural ensembles of coil and globule states by molecular dynamics simulations conducted at 273 and 323 K, respectively. We then calculate a variety of energetic and entropic components of thermodynamic quantities of the two states at the two temperatures using our recently developed, accurate statistical-mechanical method for solute hydration [1] where molecular models are employed for water and the PNIPAM structure is taken into account at the atomic level. We identify the physical factors driving or opposing the transition and evaluate their relative magnitudes and temperature dependences. The presence of PNIPAM generates an excluded volume (EV) which is inaccessible to the centers of water molecules in the entire system. The presence of a water molecule also generates an EV for the other water molecules with the result that all of the water molecules are entropically correlated, causing water crowding. The globule state, where the EV is smaller and water crowding is less significant, is more favored in terms of the translational, configurational entropy of water. This effect always opposes the globule-to-coil transition. At low temperatures, however, this effect becomes significantly weaker, yielding to the factors driving it.

(3) How does the recently discovered peptide MIP exhibit much higher binding affinity than an anticancer protein p53 for an oncoprotein MDM2? [3]

An oncoprotein MDM2 binds to the extreme N-terminal peptide region of a tumor suppressor protein p53 (p53NTD) and inhibits its anticancer activity. We recently discovered a peptide named MIP which exhibits much higher binding affinity for MDM2 than p53NTD. Experiments showed that the binding free energy (BFE) of MDM2-MIP is lower than that of MDM2-p53NTD by ~ -4 kcal/mol. Here we develop a theoretical method which is successful in reproducing this quantitative difference and elucidating its physical origins. It enables us to decompose the BFE into a variety of energetic and entropic components, evaluate their relative magnitudes, and identify the physical factors driving or opposing the binding. It should be applicable also to the assessment of differences among ligands in the binding affinity for a particular receptor, which is a central issue in modern chemistry. In the MDM2 case, the higher affinity of MIP is ascribed to a larger gain of translational, configurational entropy of water upon binding. This result is useful to the design of a peptide possessing even higher affinity for MDM2 as a reliable drug against a cancer.

(4) Elucidation of cosolvent effects thermostabilizing water-soluble and membrane proteins [4]

Thermostability of a water-soluble protein becomes higher with an increase in the gain of translational, configurational entropy of the solvent upon protein folding at 298 K. The gain, which is significantly large when the solvent is water, can be made even larger by the cosolvent addition. We previously proposed a measure evaluating the enhancement of thermostability achieved by the cosolvent addition. The measure becomes larger as the total packing fraction of the solvent increases. In this study, we predict that the measure follows the order, sucrose > glucose ~ mannitol > erythritol > glycerol. The addition of 2-propanol lowers the thermostability. These theoretical predictions, which are almost independent of the water-soluble protein species, coincide with the experimental observations. We then argue that they are applicable to membrane proteins for which not only the hydrocarbon groups in nonpolar chains of lipid molecules or in surfactant molecules of detergents but also water molecules play essential roles in protein folding. For membrane proteins solubilized in detergents, for example, closer packing of water and cosolvent molecules is also accompanied by that of the hydrocarbon groups, enlarging the entropy gain for the hydrocarbon groups upon protein folding and enhancing the thermostability. We experimentally examine the above argument for two representative membrane proteins. It is corroborated for both of them that the thermostability is actually enhanced by the sugar or polyol addition and the degree of enhancement follows the order described above, and it is lowered by the addition of 2-propanol. The cosolvent effects, especially those leading to enhanced thermostability, can be comprehended for both of water-soluble and membrane proteins by the same theory.

(5) How does a microbial rhodopsin RxR realize its exceptionally high thermostability with the proton-pumping function being retained? [5]

We often encounter a case where two proteins, whose amino-acid sequences are similar, are quite different with regard to the thermostability. As a striking example, we consider the two seven-transmembrane proteins, recently discovered *Rubrobacter xylanophilus* rhodopsin (RxR) and long-known bacteriorhodopsin from *Halobacterium salinarum* (HsBR). They commonly function as a light-driven proton pump across the membrane. Though their sequence similarity and identity are ~71 and ~45%, respectively, RxR is much more thermostable than HsBR. We solve the 3D structure of RxR using X-ray crystallography and find that the backbone structures of RxR and HsBR are quite similar to each other: The root mean square deviation for the two structures calculated using the backbone C_α atoms of the seven helices is only 0.86 Å, which makes the large stability difference more puzzling. We calculate the thermostability measure and its energetic and entropic components for RxR and

HsBR using our statistical-mechanical theory. The same type of calculation is independently performed for the portions playing essential roles in the proton-pumping function, helices 3 and 7, and their structural properties are related to the probable roles of water molecules in the proton-transporting mechanism. We succeed in elucidating how RxR realizes its exceptionally high stability with the original function being retained. This study provides an important first step toward the establishment of a method correlating microscopic, geometric characteristics of a protein with its thermodynamic properties and enhancing the thermostability through amino-acid mutations without vitiating the original function.

(6) Hydration properties of a protein at low and high pressures: Pressure denaturation [6]

Using experimentally determined structures of ubiquitin at 1 and 3000 bar, we generate sufficiently large ensembles of model structures in the native and pressure-denatured states by means of molecular dynamics simulations with explicit water. We calculate the values of a free-energy function (FEF), which comprises the hydration free energy (HFE) and the conformational energy and entropy, for the two states at 1 and 3000 bar. The HFE and the conformational entropy, respectively, are calculated using our statistical-mechanical method which has recently been shown to be accurate [1] and the Boltzmann-quasi-harmonic method. The HFE is decomposed into a variety of physically insightful components. We show that the FEF of the native state is lower than that of the denatured state at 1 bar, whereas the opposite is true at 3000 bar, thus being successful in reproducing the pressure denaturation. We argue that the following two quantities of hydration play essential roles in the denaturation: the WASA-dependent term in the water-entropy loss upon cavity creation for accommodating the protein (WASA is the water-accessible surface area of the cavity) and the protein-water Lennard-Jones interaction energy. At a high pressure, the mitigation of the serious water crowding in the system is the most important, and the WASA needs to be sufficiently enlarged with the increase in the excluded-volume being kept as small as possible. The denatured structure thus induced is characterized by the water penetration into the protein interior. The pressure denaturation is accompanied by a significantly large gain of water entropy.

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High-Temperature Plasma Equipment Engineering Research Section

H. Okada, Associate Professor

1. Introduction

The major subjects are to study fast-ion confinement in plasma confinement devices and to investigate interactions between fast-ions and materials, such as a first wall and a vacuum vessel. The fast-ion confinement is a critical issue for the fusion reactor since the alpha particles produced in the D-T reaction should be utilized to heat plasma efficiently. Fast-ion profile and velocity distribution are investigated using ion cyclotron range of frequency (ICRF) minority heating in Heliotron J with special emphasis on the effect of the toroidal ripple of magnetic field strength ('bumpiness'). In fusion reactors, fuel must be supplied since fuel particles decrease via the fusion reactions and escape continuously from the core plasma. Fueling using hydrogen-ice pellet is also our subject to generate high-density plasmas. This method is considered to have an advantage for core-plasma fueling. A small-size and slow-speed injector has been developed for plasmas in Heliotron J and the measurement system for the plasmoid formed around a pellet inside plasma has been prepared.

2. Study of Fast-ion Generation by Combination Heating of ICRF and NBI in Heliotron J

Main purpose of this study is to optimize fast ion confinement by using ICRF heating in a helical axis heliotron device, Heliotron J based on results of helical devices. For the research of the fast ion confinement in a three dimensional magnetic field, fast ions are generated by ICRF minority heating in combination with neutral beam injection (NBI) heating in Heliotron J ($R_0 = 1.2$ m, $a = 0.1$ - 0.2 m, $B_0 \leq 1.5$ T). The high energy ions are easily generated in this ICRF heating scheme. Under the same condition of target plasmas, the generation of high-energy minority ions is different for the various magnetic configurations. The high bumpiness configuration has an advantage for the formation and confinement of fast ions. The energy spectra of minority protons are illustrated in Fig.1 for NBI+ECH case and ICRF imposed case. The energy of NB injected ions is 25 keV. The spectrum before ICRF pulse injection is illustrated as circles in Fig. 1. The measurement is made using the charge-exchange neutral analyzer. Three peaks in the energy spectrum

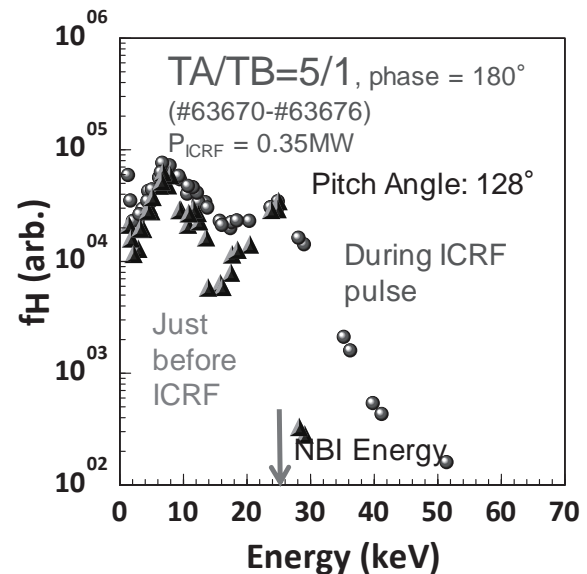


Fig.1 Measured energy spectra of minority protons before ICRF pulse injection (circles) and during that (triangles) in the experiment. Target plasmas are produced by electron cyclotron heating (ECH) and maintained by ECH+NBI.

are found near the injection energy, a half of it, and a third. The energy spectrum is extended in the high energy region after ICRF pulse is injected. The high energy ions up to 50 keV are detected. The pitch angle of the measured particles is 128° in this figure, and the pitch-angle dependence is clearly observed.

The measurement area in the experiment is limited because of the observation port arrangement. A Monte-Carlo calculation can be one of suitable tool for the handling the ions in the complicated magnetic field structure under the Coulomb collision and radio-frequency wave-particle interaction. Using Monte-Carlo method with the experimental magnetic field and plasma parameters, ICRF acceleration of NBI particles has been performed in order to estimate the averaged behavior in whole torus for various configurations. The birth position of the NBI particles (hydrogen) is calculated using NFREYA code with experimental plasma parameters. Two-dimensional velocity distribution for minority hydrogen is presented in Fig. 2. The injection energy

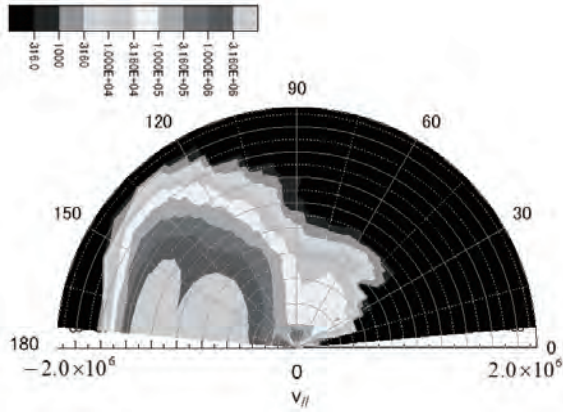


Fig.2 Calculated minority hydrogen velocity distribution during ICRF pulse. Distribution is illustrated as the velocity and pitch angle. Horizontal axis corresponds to the velocity component in the magnetic field direction.

of NBI is 25 kV and the component ratios are assumed to be 0.8 for H, 0.15 for H₂, and 0.05 H₃, respectively. The line-averaged electron density is $1 \times 10^{19} \text{ m}^{-3}$, center electron temperature is 700 eV, center ion temperature is 300 eV, and the magnetic configuration is standard. The calculated data has peak profile at the injected energy and pitch angle. The beam is diverged in velocity space through the Coulomb scattering and ICRF wave acceleration, and some ones reach the vacuum chamber wall. In Fig. 3, calculated energy spectra for several pitch-angle ranges are plotted for the comparison to the experimental data in Fig. 1. The data for the pitch angle between 120° to 130° in Fig. 3 is almost identical to the experiment data except that the peak

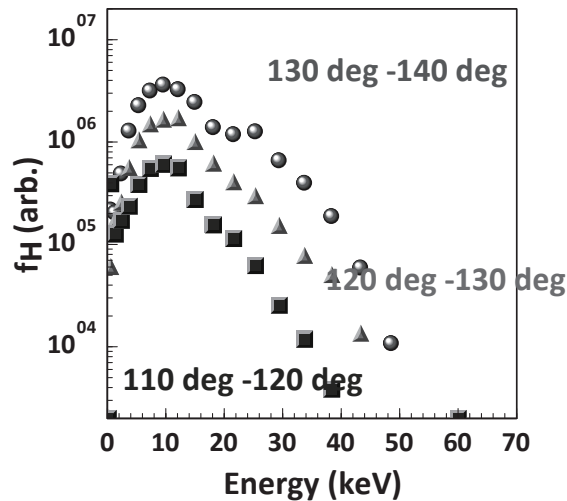


Fig.3 Calculated energy spectra of minority proton for the three pitch angle cases. The basic data is the same as Fig. 2.

at the injection energy is not clear. The beam component ratio assumed may not correct or the line of sight dependence is not negligible.

3. Study of Density Control Using Hydrogen Ice-Pellet Injection

The ice-pellet injection system has been developed for the new particle supply method following the supersonic molecular beam injection (SMBI) under the bilateral collaboration program in Heliotron J. This method is effective specially to supply particles into the plasma core region. The conditions of the pellet injector are injection speed is less than 300 m/s, and the diameter is less than 1 mm for the plasma parameters of Heliotron J. The pellet injection method is pneumatic propulsion using high-pressure helium gas.

The injection test has been successfully done for hydrogen pellet and deuterium pellets. The pellet is injected into NBI+ECH plasma and NBI-only plasma. The increase of electron density has been observed and its value was $4.0 \times 10^{19} \text{ m}^{-3}$ and the stored energy was also increased. In NBI-only plasma, the center-peaked density profile was achieved after pellet injected. The pellet penetration in NBI+ECH plasma is up to the plasma axis, whereas, the longer penetration is observed in the NBI-only plasma. The observed penetration length is probably influenced by the existence of fast electrons in NBI+ECH plasma.

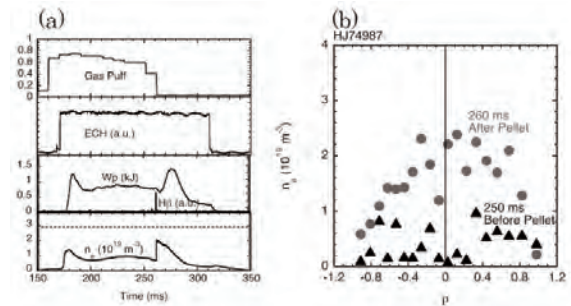


Fig. 4 (a) Time evolution of gas-puff signal, ECH pulse, stored energy, H_β signal, and line-averaged density. (b) electron density radial profile measured by Thomson scattering system before pellet injection and after that.

The density radial profile is mostly flat in ECH plasma for Heliotron J using ordinary gas-puff fueling. Pellet fueling enables making center-peaked profile because of center fueling property of pellet. This is the first observation of center-peaked density profile for the ECH plasma. Figure 4 shows time evolution of main plasma parameters and density profiles before pellet injection and after that. The peaked density profile is observed using Thomson scattering measurement as in Fig. 4 (b).

Collaboration Works

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長崎百伸, 大島慎介, 岡田浩之, 南貴司, 小林進二, Stuttgart Univ., CIEMAT (スペイン), 先進閉じ込め配位

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Environmental Microbiology Research Section

T. Hara, Program-Specific Professor

Y. Takatsuka, Program-Specific Associate Professor

1. Introduction

There is a very close relationship between the consumption of energy resources and environmental protection, which is becoming an important issue for developing a sustainable society. We still heavily rely on fossil energy, and there is concern that emitted greenhouse gases break the harmony of the global environment. In addition, we need a great deal of energy to fix environmental pollution that continues to be the shadow of the civilization's progress due to the energy consumption of fossil fuels. As one of the solutions, we will develop a practical method using 'enzymes' derived from environmental microorganisms with high efficiency of energy utilization in catabolism. In 2018, our research section has been established as a donation department and works with academisms, biotechs and university start-ups to aim for networking of researches toward social implementation of our technologies.

2-1. Two-compositely microbial catalyst efficiently degraded polychlorinated biphenyls.

Polychlorinated biphenyls (PCBs) are well-known environmental pollutants and dispersed in all our living environments. Biphenyl dioxygenase (BDO) plays a crucial role in the degradation of PCBs. BDO catalyzes the incorporation of two oxygen atoms into the aromatic ring of PCB, which induces the aromatic ring

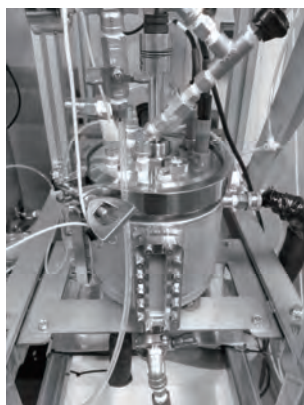


Figure 1. The composite BDOs-microbial catalyst was evaluated in the dedicated experimental bioreactor with the device of oxygen microbubble generation.

cleavage. We developed the composite type of cata-

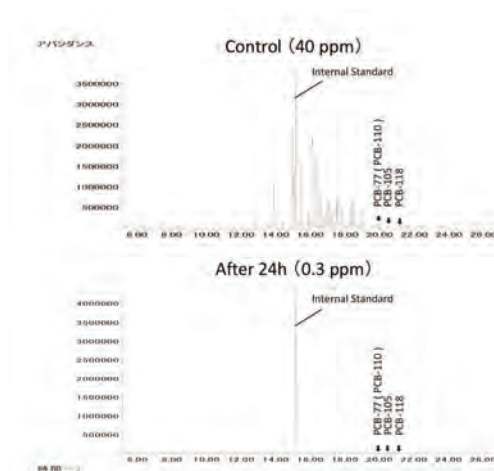


Figure 2. The data from gas chromatograph quadrupole mass spectrometer showing the PCBs degradation by the composite BDOs-microbial catalyst.

lytic enzyme with two BDOs that having different substrate specificities, and the bioreactor for generating oxygen microbubbles that enhance the enzymatic activities of BDOs (Figure 1). As a result, we succeeded in constructing a practical system combining catalytic enzymes and microbubbles, that degraded 99.3% of 40 mg L⁻¹ of major commercial PCBs (Kenechrol KC-300 and KC-400) in 24 hours (Figure 2). This result achieved the waste disposal standard defined by the Ministry of the Environment of Japan.

2-2. Several bacterial species associated with PCBs dechlorination were genetically identified on PCBs contaminated site.

In order to extend further the composite degrading reaction of PCBs, we have been trying to create a unique artificial enzyme that dechlorinates PCBs by two-electron reduction. Here, we collected fresh-water sediments from the PCBs-contaminated site in the Osaka area and investigated whether the bacteria associated with PCBs dechlorination exist. It has resulted in finding *Dehalobacter* sp. and *Desulfitobacterium* sp. by 16S rRNA gene phylogenetic analysis. It was reported that '*Dehalobacter*' dechlorinates penta-/hexa-chlorinated biphenyls[1] and '*Desulfitobacterium*' dechlorinates tetra-chlorinated biphenyls

hydroxylated at the para position[2]. In 2018, we succeeded in preparing the media for growing these particular bacterial species and their cultivation method. Furthermore, in 2019, we observed that these two bacterial species reducing PCBs in the artificially reproduced model of PCBs-contaminated environment. Even now, long-term observations are being made to confirm that these results are correct.

3-1. The biological enzymatic pesticide may become new pesticide with new sterilizing mechanism to replace the organic synthetic chemicals.

Many plant diseases are generally caused by either ascomycetes or basidiomycetes that belonging to filamentous fungi. 'Filamentous fungi' are hyphae, and proliferate to mycelia. The cell wall is a peculiar composite material. It incorporates a mix of cross-linked fibers and matrix components. The fibrous components of the cell wall are glucan, chitin, and mannan, and these sugar chains contribute to form a supple and solid filiform microfibril wall. Glycosidase is one of the hydrolases that catalyze the hydrolysis of glycosidic bonds in complex sugars. We are developing a new bio-macromolecular type of fungicide utilizing the hydrolysis reactions of glycosidases against fungal microfibril wall. Currently, our composite type of bacterial catalyst composed of 5 strains from class Bacilli, which produce and secrete various glycosidases, controlled 99.3% of a tomato-*Pestalotia* disease with *Pestalotiopsis* sp. (Figure 3). Glycosidases are classified

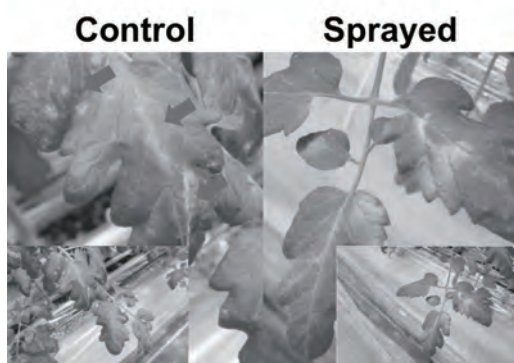


Figure 3. The glycosidase secreted type of the composite microbial catalyst inhibited tomato-*Pestalotia* disease.

into approximately 130 families, and their catalytic reactions are roughly divided into anomeric inversion and/or anomer retention, and exoglycosidase or endoglycosidase. Hence, the classification of glycosidase can be understood diverse, and we consider that it is possible to digest fungi cell wall efficiently, by compositely capably using these diversities of enzyme activities.

3-2. Phytopathogenic filamentous fungi that secrete various glycosidases kill hostile phytopathogenic filamentous fungi for their survival.

We investigated the fungicidal properties of glycosidases produced by a phytopathogenic filamentous strain belonging to basidiomycetes. This filamentous strain secretes enzymes when grown in bran medium and exhibits various glycosidase activities. The crude enzyme fraction showing such composite glycosidase activities digested 3 out of 6 wet-rice-specific epidemically filamentous fungi (Figure 4). There are not so many enzymes showing high digesting activity against multiple strains of phytopathogenic filamentous fungi.

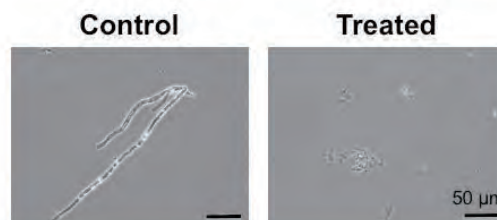


Figure 4. The crude enzyme fraction secreted from the phytopathogenic filamentous fungus digested a wet-rice specific epidemically filamentous fungal strain.

Single glycosidase activity, however, digested only 2 strains. These results suggest that glycosidases-composite have highly fungicidal activity rather than the single glycosidase activity. In fact, we try to purify components of this crude enzyme. In the near future, we will be able to clarify the effectively fungicidal mechanism of this crude enzyme by clarifying the type of the enzyme(s), the amounts of the secretion, and the specific activities.

4. Pigmented and non-pigmented *Bacillus* spores work together to improve growth, quality and health of shrimp.

In a collaborative study with Vietnam National University, we recently reported in an international journal that two strains of *Bacillus* isolated from the intestinal tract of white-leg shrimp showed excellent health-improving effects. The use of *Bacillus* probiotics is expected to help avoid the use of antibiotics and synthetic chemicals, thereby contributing to higher efficiency in food production and reducing unnecessary energy consumption.

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Collaboration Works

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Financial Support

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原富次郎, 挑戦的萌芽研究, 嫌気的自然環境で起こる有機汚染物質の脱塩素化反応を好気条件下で実現させる (分担金・エネ研・高塚)

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原富次郎, 東洋ガラス (株), 環境微生物学研究部門

原富次郎, (株) 竹中工務店, 環境微生物学研究部門

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3-2. AWARD

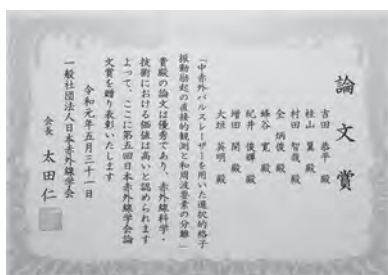
The 5th Best Paper Award of Journal of the Japan Society of Infrared Science and Technology (Japan Society of Infrared Science and Technology)

Quantum Radiation Energy Research Section
 Hideaki Ohgaki (Professor)
 Toshiteru Kii (Associate Professor)
 Heishun Zen (Assistant Professor)
 Advanced Plasma Energy Research Section
 Kai Masuda (Associate Professor)

Professor Hideaki Ohgaki, Associate Professor Toshiteru Kii, Associate Professor Kai Masuda, and Assistant Professor Heishun Zen were awarded the 5th best paper award of Journal of the Japan Society of Infrared Science and Technology from Japan Society of Infrared Science and Technology on May 31st, 2019. The best paper award of Journal of the Japan Society of Infrared Science and Technology is annually given to the best paper published in the journal. In this time, the paper entitled as “Direct observation of mode-selective phonon excitation induced by mid-infrared pulse laser with separation of the sum-frequency generation component” was awarded.

In this paper, the anti-Stokes Raman scattering light from the mode-selective excitation in 6H-SiC driven by mid-infrared free electron laser and inherently emitted sum-frequency generation light are discussed. Those lights have same wavelength and could not be separated. We found that the spectrum of the sum-frequency generation light can be estimated from the spectrum of difference-frequency generation light. Based on this result, the spectrum of sum-frequency light was separated from the anti-Stokes Raman scattering light. Then the spectrum of the anti-Stokes Raman scattering light can be evaluated.

This work was performed as a collaborative research with Dr. Kyohei Yoshida, Kumamoto University and Associate Professor Kan Hachiya, Graduate School of Energy Science, Kyoto University under the Joint Usage/Research Center for Zero Emission Energy Research, Institute of Advanced Energy, Kyoto University.



Poster Award in the 17th Summer Seminar of Material Science and Technology Division, Atomic Energy Society of Japan

Advanced Atomic Energy Research Section
 Hiroyuki Miyagaki (M2)

The 17th Summer Seminar of Material Science and Technology Division, Atomic Energy Society of Japan, which was sponsored by the Material Science and Technology Division, Atomic Energy Society of Japan, was held on 9th to 11th August, 2019 at Iwaki Business Innovation Center. This event provides young researchers and students in the field of nuclear material science an opportunity to learn about the related research regions and present their works.

Hiroyuki Miyagaki (M2) attended and made a poster presentation on the topic of “Impurity light element transport from lead-lithium eutectic using molten salt (in Japanese)”.

He received the Poster Award from the Material Science and Technology Division, Atomic Energy Society of Japan.



Poster Award in the 17th Summer Seminar of Material Science and Technology Division, Atomic Energy Society of Japan

Advanced Atomic Energy Research Section
Naoto Iwamatsu (M1)

The 17th Summer Seminar of Material Science and Technology Division, Atomic Energy Society of Japan, which was sponsored by the Material Science and Technology Division, Atomic Energy Society of Japan, was held on 9th to 11th August, 2019 at Iwaki Business Innovation Center. This event provides young researchers and students in the field of nuclear material science an opportunity to learn about the related research regions and present their works.

Naoto Iwamatsu (M1) attended and made a poster presentation on the topic of “3D monitoring of fusion neutrons using activated metals and imaging plates (in Japanese)”.

He received the Poster Award from the Material Science and Technology Division, Atomic Energy Society of Japan.

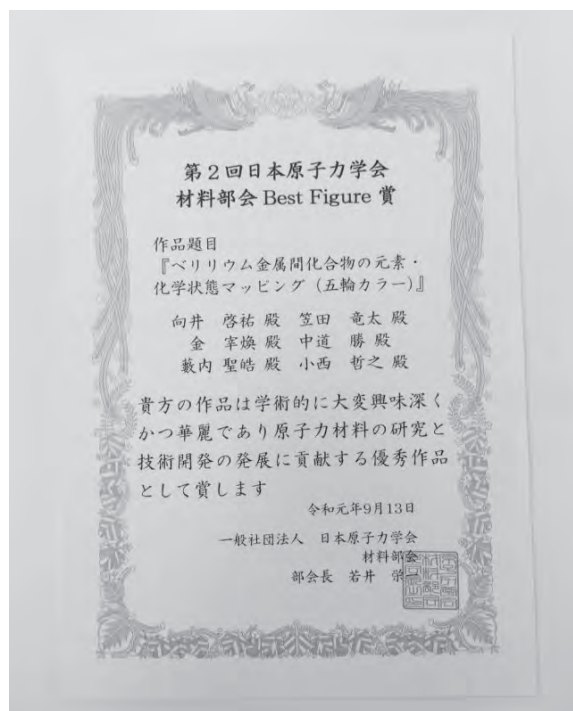


Best Figure Award in Material Science and Technology Division, Atomic Energy Society of Japan

Advanced Atomic Energy Research Section
Keisuke Mukai (Assistant Professor)

Assistant Professor Keisuke Mukai was awarded Best Figure Award from the Committee of Material Science and Technology Division, Atomic Energy Society of Japan on 13th September 2019. The Award is given for a beautiful figure which contributes to nuclear material research and development. He was awarded this prize on the figure of “Olympic colored element/chemical state maps of beryllium intermetallics”.

In his achievement, information of valence electron state was used for visualizing two dimensional distributions of beryllium intermetallics and oxide in a steamed beryllide sample which is adopted as an advanced neutron multiplier in a fusion reactor.



Student Award in 21st US-Japan Workshop on Fusion Neutron Sources and Applications

Advanced Atomic Energy Research Section
Yasuyuki Ogino (D1)

21st US-Japan Workshop on Fusion Neutron Sources and Applications (formerly on Inertial Electrostatic Confinement Fusion Workshop) was held on 17-18th December 2019 at Yoshidaizumidono, Kyoto, Japan. The international workshop is annually held in US or Japan. The student award is given to outstanding students to encourage their research activities. Yasuyuki Ogino (D1) attended and made an oral presentation on the topic of “Measurement of the Neutron Distribution with Cylindrical DD Neutron Source”. He presented results of 2-D neutron measurement by activation-foil imaging-plate method. He received the Student Award from the committee of the workshop, Prof. Gerald L. Kulcinski from University of Wisconsin.



Young Researcher Award (Institute of Advanced Energy, Kyoto University)

Advanced Atomic Energy Research Section
Keisuke Mukai (Assistant Professor)

Assistant Professor Keisuke Mukai was awarded Young Researcher Award from the director of Institute of Advanced Energy Kyoto University on 6th March 2020. The Young Researcher Award is annually given to young researchers who have achieved outstanding academic results. He was awarded this prize on the achievements of “Chemical state analysis of beryllium intermetallics using soft X-ray emission spectroscopy”. In his research, electron structures of beryllium compounds are analyzed for visualizing chemical state map of chemical phase in a steamed beryllium intermetallic specimen.



Poster Award in the Workshop on “Radiation Effects on Materials (2019)”

Advanced Energy Material Research Section
Bo Huang (Program-Specific Researcher)

This workshop is an annual program organized by Radiation effects on Materials Organization, which started from 1978 for organization of work-shop for discussion of irradiation hardening and embrittlement towards keeping better integrity of nuclear structural components. In fiscal year 2019 the workshop on “Radiation Effects on Materials” was held on 9th-10th January, 2020 at Tohoku University.

Doctor Bo Huang (Program-Specific Researcher) got awarded on his poster presentation with the topic of “Swelling and Raman Spectroscopy of C/BN Particle Dispersed SiC Materials after Ion Irradiation”. He displayed a newly-developed SiC materials dispersed with C/BN particles, and the resistance to ion irradiation of these materials.



2019 Annual Spring Heat and Fluid Working Group Excellent Presentation Award in the Atomic Energy Society of Japan

Advanced Energy Structural Materials
Research Section
Xiaoyong Ruan (D3)

The Atomic Energy Society of Japan was founded in 1959 as the only organization in Japan that aims to contribute towards progress in the development of atomic energy by seeking academic and technological advances pertaining to the peaceful use of atomic energy.

Mr. Xiaoyong Ruan is a Ph.D. student in Kyoto University, Kyoto, Japan. He made oral presentation and poster presentation at the 2019 Annual Spring Meeting. He was given the 2019 Annual Spring Heat and Fluid Working Group Excellent Presentation Award because he made an excellent presentation, and his research be applicable to engineering practice.



2019 Student Session Outstanding Achievement Award in the Japan Society of Maintenology

Advanced Energy Structural Materials
Research Section
Xiaoyong Ruan (D3)

The Japan Society of Maintenology was founded in 2003 to establish “Maintenology” of nuclear power plants, other complex artifacts, and the natural environments, emerged by collecting a wide variety of information and knowledge of engineering, technology, natural science, sociology, and so on. Mr. Xiaoyong Ruan made oral and poster presentations at the 2019 Annual Meeting. He was given the Student Session Outstanding Achievement Award because his research fits engineering practice and he made a good presentation.



2019 Annual Autumn Student Outstanding Lecture Award in the Atomic Energy Society of Japan

Advanced Energy Structural Materials
Research Section
Xiaoyong Ruan (D3)

The Atomic Energy Society of Japan was found-ed in 1959 as the only organization in Japan that aims to contribute towards progress in the develop-ment of atomic energy by seeking academic and technologi-cal advances pertaining to the peaceful use of atomic energy.

Mr. Xiaoyong Ruan is a Ph.D. student in Kyoto University, Kyoto, Japan. He made oral presentation and poster presentations at the 2019 Annual Autumn Meeting. He was given the 2019 Annual Autumn Student Outstanding Lecture Award because he made an excellent presentation, and his research has certain application value.

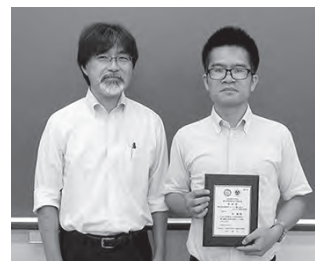


2019 Encouragement Award in Fusion Engineering Division, Atomic Energy Society of Japan

Advanced Energy Structural Materials
Research Section
Peng Song (Researcher)

The Atomic Energy Society of Japan was founded in 1959 as the only organization in Japan that aims to contribute towards progress in the development of atomic energy by seeking academic and technologi-cal advances pertaining to the peaceful use of atomic energy.

Dr. Peng Song has studied on the effects of He implantation on the oxide dispersed strengthened ferritic steels and obtained remarkable results. Finally, he was awarded the Encouragement Award in Fusion Engineering Division, Atomic Energy Society of Japan.



2019 Young Scientist Award in Materials Science and Technology Division, Atomic Energy Society of Japan

Advanced Energy Structural Materials
Research Section
Jin Gao (Researcher)

The Atomic Energy Society of Japan was found-ed in 1959 as the only organization in Japan that aims to contribute towards progress in the develop-ment of atomic energy by seeking academic and technological advances pertaining to the peaceful use of atomic energy.

Dr. Jin Gao has made lots of effort for the study on the relationship between the irradiation hardening and microstructure evolution in ferritic steels and obtained remarkable results. Finally, he was awarded the Young Scientist Award in Materials Science and Technology Division, Atomic Energy Society of Japan.

2019 Encouragement Award in Water Chemistry Division, Atomic Energy Society of Japan

Advanced Energy Structural Materials
Research Section
Yen-Jui Huang (Researcher)

The Atomic Energy Society of Japan was found-ed in 1959 as the only organization in Japan that aims to contribute towards progress in the develop-ment of atomic energy by seeking academic and technological advances pertaining to the peaceful use of atomic energy.

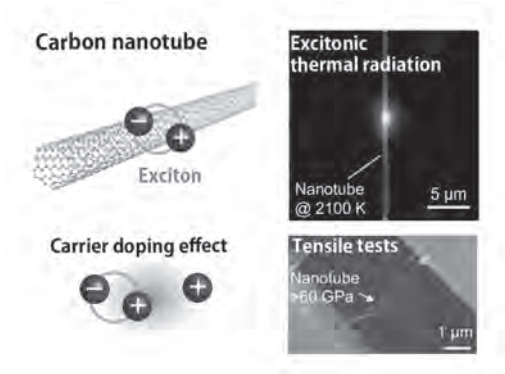
Dr. Yen-Jui Huang has studied on stress corrosion cracking (SCC) phenomenon in light water reactors. Finally, he was awarded the Encouragement Award in Fusion Engineering Division, Atomic Energy Society of Japan.

Young Scientist Award of the Physical Society of Japan, 2020

Nano Optical Science Research Section
Taishi Nishihara
(Program-Specific Assistant Professor)

Dr. Taishi Nishihara was awarded Young Scientist Award from the Physical Society of Japan on March 16th, 2020. The Young Scientist Awards are annually given to young researchers who have made outstanding achievements in their early research careers. He was awarded this prize (the division 5; optical properties of condensed matter), on the achievements of “Study of excitonic optical properties of nanocarbon materials”.

Nanocarbon materials including fullerene, carbon nanotube, and graphene have attracted much attentions from various fields owing to their unique structures and properties. He has revealed novel excitonic features of single-walled carbon nanotube, such as narrow-band thermal radiation and discrete carrier doping effect, in addition to their intrinsic outstanding strength. He also tackles the development of new nanocarbon materials with the chemists. These achievements provide significant contributions and new insights into nanocarbon science.



Young Scientist Poster Award (The Fullerenes, Nanotubes and Graphene Research Society) and Journal of Material Chemistry A Presentation Prize (The Royal Society of Chemistry)

Nano Optical Science Research Section
Kenya Tanaka (M2)

Kenya Tanaka (M2) was awarded Young Scientist Poster Award (The Fullerenes, Nanotubes and Graphene Research Society) and Journal of Material Chemistry A Presentation Prize (The Royal Society of Chemistry) of The 58th Fullerenes-Nanotubes-Graphene General Symposium on March 16th, 2020. The Young Scientist Poster Award is given to a few researchers who gave a poster presentation. The Journal of Material Chemistry A Presentation Prize is given to an outstanding presentation at the conference. He was awarded these prizes on the presentation of “Machine-learning approach for predicting low temperature valley polarization landscapes in 2D semiconductors”.

He presented new understanding of valley optical properties of atomically thin semiconductors by approaches of data driven method in the previous symposium on September 4th, 2019 at Nagoya University. In addition, this study demonstrates that interpretable machine learning analysis is an effective method for the researcher on physics and materials science.

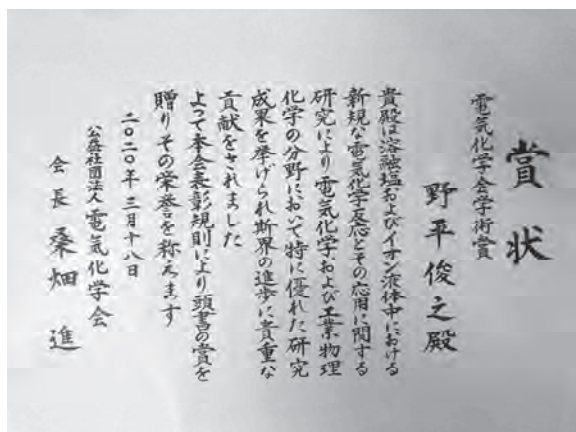


Scientific Achievement Award of The Electrochemical Society of Japan

Chemical Reaction Complex Processes
Research Section
Toshiyuki Nohira (Professor)

Professor Toshiyuki Nohira was awarded Scientific Achievement Award of The Electrochemical Society of Japan on March 18th, 2020. This award is annually given to a researcher who has made outstanding scientific achievements in the field of electrochemistry. He was awarded this prize on the achievements of “Novel Electrochemical Reactions in Molten Salts and Ionic Liquids and Their Applications”.

In his award lecture, which was held on the web on March 17th, 2020, he presented several new electrochemical reactions and their applications in molten alkali halides, alkali earth halides, and amide ionic liquids. Typical examples in molten salts are new production methods of solar grade silicon and electrodepositions of Si, Ti and W. Distinctive examples in ionic liquids are sodium and potassium secondary batteries using FSA-based ionic liquids.

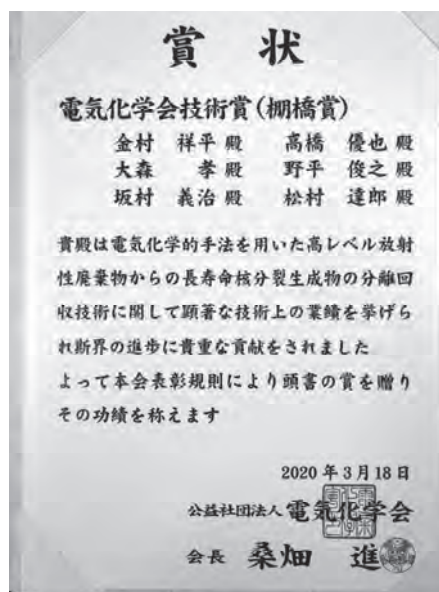


Technical Development Award of The Electrochemical Society of Japan (Tanahashi Award)

Chemical Reaction Complex Processes
Research Section
Toshiyuki Nohira (Professor)

Professor Toshiyuki Nohira was awarded Technical Development Award of The Electrochemical Society of Japan (Tanahashi Award) on March 18th, 2020. This award is annually given to researchers who have made outstanding technical development in the field of electrochemistry. He and five co-authors were jointly awarded this prize on the topic of “Application of Electrochemical Method to Recovery of Long-lived Fission Product from High Level Radioactive Waste”.

They developed a new electrochemical method to recover long-lived fission products (LLFPs) such as ^{107}Pd , ^{135}Cs , ^{79}Se , ^{93}Zr from high level radioactive wastes. The first step of this method is the electrochemical/chemical reduction of vitrified wastes in molten CaCl_2 . The second step is the separation and recovery of LLFPs by electrochemical/chemical processes.



Research Encouragement Award at The 51st Symposium on Molten Salt Chemistry

Chemical Reaction Complex Processes
Research Section
Makoto Unoki (M1)

The 51st Molten Salt Symposium, which was sponsored by the Molten Salt Committee of the Electrochemical Society of Japan, was held on 24th October, 2019 at Hokkaido University. This event provides young researchers and students in the field of molten salt chemistry and its surrounding area an opportunity to present their works.

Makoto Unoki (M1) attended and made an oral presentation on the topic of “Electrodeposition of titanium in LiF–LiCl Eutectic Molten Salt”.

He received the Research Encouragement Award from the Molten Salt Committee of the Electrochemical Society of Japan.



Student Presentation Award at 87th ECSJ Spring Meeting

Chemical Reaction Complex Processes
Research Section
Makoto Unoki (M1)

The 87th ECSJ Spring Meeting was held on the web from 17th-19th March, 2020. This event provides young researchers and students in the field of electrochemistry and its surrounding area an opportunity to present their works.

Makoto Unoki (M1) made a presentation on the topic of “Effect of Oxide Ions on Electrodeposition of Titanium in Eutectic LiF–LiCl Molten Salt”. He investigated the changes of electrochemical behavior and electrodeposits depending on the added amounts of oxide ions.

He received the Student Presentation Award from the Electrochemical Society of Japan.



Best Poster Award in the 2nd Nucleation and Growth Research Conference

Chemical Reaction Complex Processes
Research Section
Airi Kondo (M2)

The 2nd Nucleation and Growth Research Conference was held on 10th–13th June 2019 at Kansai Seminar House in Kyoto, which organized by Materials Tailoring Society and sponsored by the Electrochemical Society. The prime purpose of this conference is to discuss in-situ measurements as well as mathematical models of the relevant non-equilibrium reaction and deposition processes, in which electrons, ions, radicals, and clusters interact at the substrate surface.

In this meeting, Ms. Airi Kondo (M2) attended and made a poster presentation on the topic of “Electrodeposition of Silicon in AF–ACl (A = Li, Na, K, Cs) Molten Salts”, and received the Best Poster Award. She presented the differences of electrochemical behaviors of Si(IV) ions at a Ag electrode in eutectic molten AF–ACl (A = Li, Na, K, Cs) at 1023 K. She reported that cation species (Li^+ , Na^+ , K^+ , Cs^+) affect the Si deposition potential, and that the thermal decomposition rate of A_2SiF_6 in molten salts. The stability of Si(IV) complexes is explained by the difference of interactions between A^+ and F^- in molten salts.



Poster Award in the 84th Workshop of Materials Tailoring Society

Chemical Reaction Complex Processes
Research Section
Airi Kondo (M2)

The 84th Workshop of Materials Tailoring Society was held on 25th–27th July 2019 at Karuizawa training institute in Nagano, which organized by Materials Tailoring Society.

The purpose of this workshop is to systematize the basic science of non-equilibrium processing such as plasma and electrolysis processes, and also to apply them to energy conversion and storage systems, and new electronic and photonic processing fields.

In this workshop, Ms. Airi Kondo (M2) attended and made a poster presentation on the topic of “Electrodeposition of Silicon in AF–ACl (A = Li, Na, K, Cs) Eutectic Melts”, and received the Poster Award. She presented the differences of electrochemical behavior of Si(IV) ions at a Ag electrode in eutectic molten AF–ACl (A = Li, Na, K, Cs) at 1023 K. In molten LiF–LiCl, deposits contained Si–Li alloy. The Si electrodeposits obtained in molten NaF–NaCl were bulky, porous, and fragile. In contrast, dense crystalline Si films were obtained in molten KF–KCl and CsF–CsCl. These Si films were expected to be applied to crystalline Si solar cells.

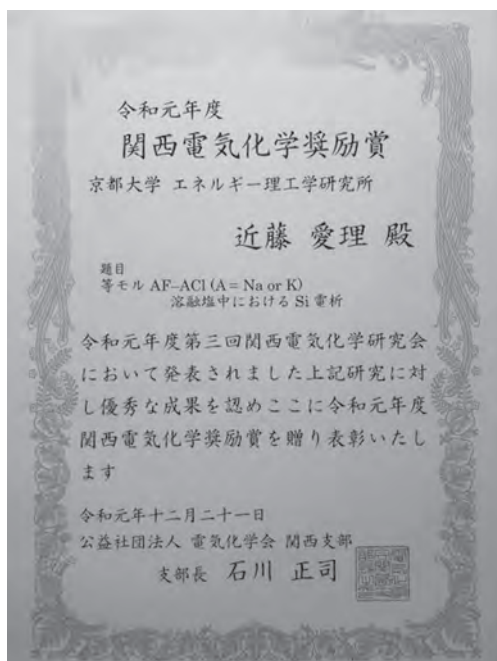


Young Researcher's Award in the 3rd Kansai Electrochemistry Workshop

Chemical Reaction Complex Processes
Research Section
Airi Kondo (M2)

The 3rd Kansai Electrochemistry Workshop was held on 21st December 2019 at Kyoto University, which was held by the Kansai Branch of the Electrochemical Society of Japan. This event provides young researchers and students in the field of electrochemistry and its surrounding area an opportunity to present their works.

In the meeting, Ms. Airi Kondo (M2) attended and made a poster presentation on the topic of "Comparison of Silicon Electrodeposition in Equimolar AF-ACl (A = Na or K) Molten Salts", and received the Young Researcher's Award. She investigated the effects of cations on silicon electrodeposition in equimolar AF-ACl (A = Na or K) molten salts at 1073 K. Fragile Si wires deposited in NaF-NaCl. On the other hands, dense crystalline Si films were obtained in molten KF-KCl, which is expected to be applied to solar cells. She also investigated morphologies of the Si deposits obtained with various depositing times by SEM. She revealed that the growth mechanisms of Si deposits are different between molten NaF-NaCl and KF-KCl.



Best Poster Award in the 11th International Conference on Molten Salts Chemistry and Technology

Chemical Reaction Complex Processes
Research Section
Yutaro Norikawa (D3)

The 11th International Conference on Molten Salts Chemistry and Technology was held on 19th–23rd May 2019 in Orléans, France. This conference provides many researchers in the field of molten salts and its surrounding area an opportunity to present their works.

In this conference, Mr. Yutaro Norikawa made a poster presentation on the topic of "Electrodeposition of Ti from Water-Soluble KF-KCl Molten Salt Containing Ti(III) Ions". He presented the electrochemical behavior of Ti(III) ions and the optimal conditions for Ti film electrodeposition. The electrodeposited Ti films had good adhesion and compact and smooth surface. His poster was evaluated highly and awarded the Best Poster Award.



Best Poster Award in the 2nd Nucleation and Growth Research Conference

Chemical Reaction Complex Processes
Research Section
Yutaro Norikawa (D3)

The 2nd Nucleation and Growth Research Conference was held on 10th–13th June 2019 at Kansai Seminar House in Kyoto, which organized by Materials Tailoring Society and sponsored by the Electrochemical Society. The prime purpose of this conference is to discuss in-situ measurements as well as mathematical models of the relevant non-equilibrium reaction and deposition processes, in which electrons, ions, radicals, and clusters interact at the substrate surface.

In this conference, Mr. Yutaro Norikawa made a poster presentation on the topic of “Effect of Temperature on Electrodeposition of Ti Films in Fluoride–Chloride Mixture Melt”. He presented the effect of temperature on the electrochemical behavior of Ti(III) ions and the morphology of electrodeposited Ti. The diffusion coefficient of Ti(III) ions became higher according to the temperature increase. Rapid diffusion of Ti(III) ions is advantageous for obtaining smooth Ti films. He found that Ti films with smooth surface were obtained at lower temperature. This result was explained by that the temperature-dependent crystal growth rate is important for electrodepositing smooth Ti films. From these findings, he was awarded the NGRC Best Poster Award.



Student Award in IAE, Kyoto University (2019)

Biofunctional Chemistry Research Section
Huyen Dinh
(Program-Specific Assistant Professor)

This award is conferred annually for excellent students of the Institute of Advanced Energy, Kyoto University, who gained superior achievements in their research under supervision of professors in the institute.

Huyen Dinh (Project-specific Assistant Professor) studied on enzyme reactions in the ordered assembly states. In this topic, the enzyme carbonic anhydrase was assembled on a DNA nanostructure with the controlled numbers and distances. When in a packed state with the distance of less than 1 nm, the enzyme showed faster reaction rate than in a dispersed state on DNA scaffold as well as in a free solution. More experiments were done in order to explain the acceleration of the reaction in the packed assembly of enzyme, which would be helpful in engineering artificial metabolic systems.



Early Career Presentation Award in The 57th Annual Meeting of the Biophysical Society of Japan

**Structural Energy Bioscience
Research Section
Yudai Yamaoki (Researcher)**

The 57th Annual Meeting of the Biophysical Society of Japan was held on from 24 to 26 September, 2019 at Seagaia, Miyazaki. This meeting is an annual domestic meeting of biophysicists in Japan and provides a place for exchanging knowledge, methods and techniques to understand biological phenomena by applying physical techniques.

In this meeting, Yudai Yamaoki made oral presentation entitled “Evaluation of the structure and dynamics of nucleic acids inside the living human cells by in-cell NMR spectroscopy”. Inside the living cell is highly dense with biomolecules. The properties of nucleic acids can be different between dilute aqueous solution such as *in vitro* conditions and intracellular crowded conditions. In-cell NMR is a robust method for the direct measurement of those properties of biomolecules in the living cells. In his presentation, the first successful observations of in-cell NMR signals of nucleic acids in living human cells were reported. These measurements provided the insights for the structures and dynamics of nucleic acids in living human cells.

Yudai Yamaoki was awarded Early Career Presentation Award from the Biophysical Society of Japan. Early Career Presentation Awards was established to promote the activity of young researchers and is annually given to 10 researchers who show their great potential to contribute to the progress of biophysics.



4. JOINT USAGE/RESEARCH PROGRAM



Joint Usage/Research Center Program “Zero Emission Energy Research”

It is an urgent task to find out the best solutions against the energy and environmental problem for ensuring the sustainable society on the earth. The new energy system for this purpose has to be an environmentally friendly or ecological one. Here, we should consider not only the energy sources but also the efficiency in the each phase of energy usage. The former should have good quality and enough quantity. The latter should be considered including the so-called “three Rs (Reduce, Reuse and Recycle)” in the energy system;

- Reduce of energy consumption, environmental pollutant such as greenhouse gas, waste-heat, hazardous waste, etc.
- Reuse of waste heat/energy, etc.
- Recycle of fuel, etc.

In order to realize them, only the extension of the present technology is not enough. Interdisciplinary studies with innovative ideas are indispensable to realize the energy system for next generation.

We propose a new concept of Zero Emission Energy as a typical model of Advanced Energy. IAE Zero Emission Energy Research aims at the realization of environmentally friendly energy system for sustainable society with minimum emission of environmental pollutants and with maximum utilization of energy and resources. Since FY2011, we had operated a project, “Joint Usage/Research Program on Zero Emission Energy”, which is the program authorized by the MEXT. We have started the second term of the Program from FY2016. Here, we aim to (1) promote interdisciplinary joint usage/research studies for

Zero Emission Energy Science & Technology, (2) promote education & practical training for young researchers and (3) explore future horizon of Advanced Energy System for sustainable development. IAE provides many unique & attractive facilities for the Joint Usage/Research not only in the field of advanced plasma & quantum energy but also in the field of soft energy.

Many researchers have participated in this program. In FY2019 Joint Usage/Research collaborations of total 107 subjects (including one workshop) on Zero Emission Energy were performed with more than 462 visiting participants from 64 all-Japan Universities and Institutions including graduate/undergraduate students. Researchers from 8 foreign Universities also participated in the program. The results of these collaborations are summarized in a report "IAE Joint Usage/Research Program on Zero Emission Energy 2019". The meeting to present some of remarkable results obtained in FY2019 was planned to be held at Uji Campus on March 9, 2020. Unfortunately, it was canceled due to the spread of infection of new coronavirus. If you have interest to this collection, please contact to the Office of Zero Emission Energy Research.

In addition to the Joint Usage/Research collaborations, we organized "The 10th International Symposium of Advanced Energy Science -Beyond the Decade of Zero Emission Energy-" on September 4–6, 2019 at Uji Obaku Plaza, Kyoto University. This symposium consists of oral and poster sessions, panel discussion, parallel seminars and satellite meeting. 383 scientists and students including 6 foreign and 13 domestic invited speakers were participated in the symposium. In addition, several informal seminars and/or internship on Zero Emission Energy were also organized. (http://www.iae.kyoto-u.ac.jp/zero_emission/calendar/)

We are also operating “Zero Emission Energy Network” to share the knowledge of Advanced Energy and Zero Emission Energy with researchers in the fields of energy science and technology, since world-wide activities for Zero Emission Energy Research are indispensable for the realization of sustainable society.

In FY2018, the intermediate examination by MEXT was conducted for all the Joint Usage/Research Center Programs. Our program was given "A" evaluation. Since then, we have been continuing the effort to keep this high evaluation with the researchers of the related communities.



Poster of the 10th International Symposium

List of Zero Emission Energy Joint Usage/Research Subjects in FY 2019

(Subject, Principal Researcher, IAE Key Person)

Improvement of Protonic Properties of Hydronium Solvate Ionic Liquids, A. Kitada, M. Katahira

Standardization of Ion-Irradiation Field, R. Kasada, K. Yabuuchi

Study of formation process of solute clusters in stainless steel with ion irradiation, K. Fukumoto, K. Yabuuchi

Development of an eco-conscious amination process for functionalization of cellulose biomass, M. Takeda, M. Katahira

Crystal Growth of Silicon from Liquid Si-Zn alloy for the Production of Solar-grade Silicon, K. Yasuda, T. Nohira

Photoinduced electron-transfer reactions of metal complexes as photosensitizers bound to the active site of enzyme, H. Takashima, E. Nakata

Development of anode/electrolyte interface for advanced Na-ion battery, H. Sakaguchi, T. Nohira

Study on development of compound-based anode for K-ion battery and on compatibility with molten salt electrolyte, Y. Domi, T. Yamamoto

Effects of Magnetic Field and Metal Nanoparticles on Photoproperties of Dye-Metal Nanoparticle Composite Films, H. Yonemura, H. Sakaguchi

Design and development of functional organic materials for energy conservation-directed light-emitting devices, M. Shimizu, H. Sakaguchi

Development of a compact THz laser and its applications using energy-chirping-cell attached rf electron gun, K. Sakaue, H. Zen

Development of hyper-efficient degradation method of biomass-related compounds by using mid-infrared free electron laser, T. Kawasaki, H. Zen

Development of thermal diffusivity evaluation method using miniature laminated specimens, M. Akiyoshi, T. Hinoki

Valence electric structures of oxidation resistant beryllides, M. Nakamichi, K. Mukai

Feasibility study and development of novel technique of measuring transverse velocity field using optical vortex emitted from photonic crystal laser, H. Himura, S. Kado

Stability of oxide particles in oxide dispersion strengthened (ODS) alloys under irradiation, N. OONO-HORI, K. Yabuuchi

Mode-selective phonon excitation in semiconductors of energy functionality with mid-infrared free-electron laser, K. Hachiya, H. Ohgaki

Photoenergy Conversion System Based on Hybrid DNA/Inorganic Nanomaterials, K. Yamana, T. Morii

Development of radiation measurement method for the detection of special nuclear materials with IEC device, T. Misawa, S. Konishi

Electrodeposition of Si films in molten salts for low-cost manufacturing of solar cells, X. Yang, T. Nohira

Analysis of transition from axisymmetric torus to helical axis toroidal plasma, A. Sanpei, K. Nagasaki

Synergistic effects of electronic excitation and displacement damage in oxide/nitride ceramics, K. Yasuda, K. Yabuuchi

Combined effect of high-temperature irradiation with heavy ion and helium on hydrogen permeation behavior in functional coating for fusion reactor blanket, T. Chikada, K. Yabuuchi

Valence electron structure of Li-containing ceramic breeder for fusion application, K. Sasaki, K. Mukai

Influence of alloying elements on radiation damage formation and hydrogen isotope trapping in tungsten, Y. Hatano, T. Hinoki

Development of Organic-Inorganic Hybrid Film toward High-Performance Organic Thin-Film Solar Cells, T. Akiyama, H. Sakaguchi

Development of high ductile ODS ferritic steel for advanced energy system, N. Iwata, K. Yabuuchi

High-Fluence Irradiation Behavior of Reduced Activation Fusion Reactor Materials, H. Tanigawa, T. Hinoki

Modeling and Experimental Study on Damage Rate Effects on Bubbles/Voids Formation in Fusion Reactor Structural Materials, T. Yamamoto, K. Yabuuchi

Effect of high energy He ion implantation on hydrogen isotope behavior in tungsten, Y. Oya, T. Hinoki

Hydrogen Isotope Retention in Tungsten by Continual Pulsed Plasma Irradiation in Fusion Reactor, Y. Ueda, T. Hinoki

Study of high energy particle irradiation effects on Tungsten materials for fusion applications, A. Hasegawa, K. Yabuuchi

The role of lattice defects in ceramics on the corrosion, S. Kondo, T. Hinoki

Evaluation of the stability of irradiation induced point defect clusters during annealing, S. Jitsukawa, T. Hinoki

Strengthening and improvement of ductility by precipitation control for low-activation vanadium alloy for fusion reactors, T. Nagasaka, K. Yabuuchi

Maximizing energy production from a household grid-connected PV system in Phnom Pehh, Cambodia, V. Vai, H. Ohgaki

Interaction analysis between cellulase carbohydrate-binding module and lignin by ultra-high sensitivity NMR for biorefinery, T. Watanabe, M. Katahira

Elucidation of exciton formation and dissociation processes exclusively in polymer crystalline domain, featuring high-degree of molecular ordering in ultrafast time-scale, J. Park, K. Matsuda

Development of a system that induces Ribosomal Shunting, Y. Katsuda, T. Morii

Study of Hydrogen Isotope Separation Technology by Molten Salt, H. Matsushima, T. Nohira

Identification and characterization of novel antimicrobial cyclic lipopeptides derived from *Bacillus* sp. , K. Yokota, T. Hara

Thermal properties of sugar alcohol phase change material, M. Shibahara, T. Hinoki

Influence of Wire Spacer on Natural Convection Heat Transfer from Vertical Rod Bundle in Liquid Metal (Part 2), K. Hata, T. Nakajima

Analysis of high-speed camera data based on magnetic flux information, N. Nishino, H. Okada

Highly efficient photochemical reactions induced by optimal laser pulses, Y. Ohtsuki, T. Nakajima

Effect of the orientation of poly(lactic acid)/zinc oxide electrospun fibers on the antimicrobial properties, T. Jamnongkan, T. Hara

Development of functional peptides and RNAs by using NMR, T. Sakamoto, T. Nagata

Higher vibronic excited states of bridging cyanides in prussian blue realized by ultra short pulse train from a mid infrared free electron laser, M. Kitaura, H. Zen

Development of HeI image reconstruction technique using neural network in Heliotron J, H. Kawazome, S. Kado

Behavior of hydrogen on the surface of fusion reactor materials by computer simulations, H. Iwakiri, K. Morishita

Study of electron bunch length by measuring coherent synchrotron radiation with narrow-band detectors, N. Sei, H. Ohgaki

Development of single-electron irradiation technique for microscopic track structure study, Y. Uozumi, H. Ohgaki

Observation of fine temperature structure by using digital ECE, S. Inagaki, K. Nagasaki

Analysis of radiation induced nano-cluster in RPV steels, H. Watanabe, K. Yabuuchi

Analysis of reaction mechanism of haloacid dehalogenase, T. Nakamura, T. Morii

Structural studies on hierarchical molecular architectures created in microfluidic device, M. Numata, E. Nakata

R&D of BN/CNTs heat dissipation sheets as heat transfer, K. Shimoda, T. Hinoki

Development of an RNA editing technology for regulating an intracellular energy production system, M. Fukuda, T. Morii

Study on the microbial community structure in medical plant and its application to biological pesticides, M. Ueno, T. Hara

Cooperative effects of pigmented and non-pigmented *Bacillus* spores on growth, quality and health of shrimp, A. Nguyen, Y. Takatsuka

Production and transport control of reactive radicals with atmospheric pressure plasma, H. Matsuura, S. Kado

Analysis of the mechanism of ultrasound-enhanced cellular internalization of bioactive molecules, T. Ohtsuki, E. Nakata

Nondestructive evaluation of residual elastic strain on non-irradiated areas by defects caused by ion irradiation, T. Shibayama, T. Hinoki

Clarification on retention processes of He and H in ion irradiated pyrochlore oxides, B. Tsuchiya, T. Hinoki

Measurement of the ablation threshold fluence of materials interacted with intense THz waves and mid-infrared laser, M. Hashida, H. Zen

Effect of irradiation on explosion bonded Cu/steel joint, S. Ohnuki, K. Yabuuchi

Effect of hydrogen on surface hardness in ion-irradiated tungsten, K. Sato, K. Yabuuchi

Staple Antisense-Induced RNA Folding for Specific Gene Regulation, M. Hagihara, T. Morii

Development of quadruplex-based gene expression regulation method, Y. Tanaka, T. Nagata

Fabrication of 2D-3D hybrid quantum well structure towards energy conversion devices, S. Mouri, K. Matsuda

Physical properties of heterostructures of 2D materials, S. Okada, K. Matsuda

Supramolecular assembling regulation of bacterial cell division protein FtsZ on DNA nanostructures, A. Onoda, E. Nakata

Development of intracellular thermosensors for the understanding of energy production in mitochondria, R. Sakaguchi, T. Morii

Spatially resolved measurement of helium atom 23S-23P emission line intensity using near-infrared Zeeman spectroscopy, T. Shikama, S. Kado

Research for improving the efficiency of hydrogen release from titanium hydride particles, Y. Kajimura, J. Yagi

A small-molecule-based technology for live-cell imaging of energy metabolism, S. Sato, T. Morii

Real-time NMR analysis of the continuous degradation process of azo dyes using azoreductase in cooperation with the NADPH regeneration system, M. Horiuchi, T. Nagata

Digital Imaging Spectrometry for Visible Spectra in Fusion Plasma Based on the Atomic/Molecular Process, M. Irie, S. Kado

Nanopore formation by electrochemical dissolution of SiC caused by selective activation of lattice vibration, K. Fukami, M. Kinoshita

Study of nanomaterials toward efficient and high-performance energy conversion, S. Konabe, Y. Miyauchi

Study of high performance plasmas using neutral beam injection in advanced heliotron configuration, M. Yoshikawa, S. Kobayashi

Modeling and simulation study on radiation damage of reduced activation ferritic/martensitic steel for fusion application, Y. Watanabe, K. Morishita

Design and construction of external stimuli-responsive protein materials, Y. Suzuki, E. Nakata

Evaluation of effect of condensation heat transfer on wall temperature under high pressure conditions, Y. Yamamoto, K. Morishita

Mechanical Property of Ion-irradiated RAFMs by Ultra Micro-tensile Test, M. Ando, K. Yabuuchi

Study on Rural Electrification by Renewable Energy in Sarawak and its Impact on QOL, N. Rahim, H. Ohgaki

Generation of high energy density plasma state by the interaction between highly ordered silicon rod array target and high power laser, Y. Kishimoto, H. Sakaguchi

Development of multi-channel spectroscopic system for turbulence measurement, A. Fujisawa, S. Ohshima

Iontronic devices using dynamic heterogeneous phase, N. Yonekura, T. Nakajima

Development of reduced activation high entropy materials for high energy reactor, N. Hashimoto, K. Yabuuchi

Development of novel laser nanoprocessing with Bessel-like few-cycle laser pulses, G. Miyaji, K. Matsuda

Exploitation of Lignin- and Cellulose-Binding Peptide Library toward Biorefinery of Wood Biomass, H. Takaya, T. Morii

Search for nonlinear effects of solid using KU-FEL, A. Irizawa, H. Zen

Lithium distribution analysis for the corrosion of liquid breeding material using soft X-ray spectrometer, T. Tanaka, J. Yagi

Excess Capacity and Reaction Mechanism of Fe_2O_3 - Al_2O_3 Solid Solution Anode at the Al-rich Region, S. Takai, T. Morii

Study on emission process of scintillation material using the one electron beam and evaluation of scintillation properties for darkmatter search, S. Kurosawa, H. Ohgaki

Statistical analysis on edge turbulence fluctuation data in a toroidal plasma, Y. Nagashima, S. Ohshima

Artificial reconstruction of cyanobacterial phycobilisome, S. Watanabe, E. Nakata

Bio-Physical Reactions of Crayfish's Compound Eye Stimulated by Mid-Infrared Radiation of Free-Electron Lasers, F. Shishikura, H. Ohgaki

Saturation of an infrared semiconductor detector and pulse structure of a light source, Y. Ikemoto, H. Zen

Boundary diagnostics using field corresponding double probe in Heriotron J, K. Uehara, S. Ohshima

Study for polarization control of coherent THz undulator radiation, S. Kashiwagi, H. Zen

Enhancement of carbon dioxide gas fixation in the atmosphere by promoting shell formation of snails (gastropoda), T. Kono, H. Ohgaki

Determination of the free energy of the late-blooming phase, Y. Matsukawa, K. Yabuuchi

TEM-STEM Characterization of Oxide Nanoparticles in ODS Steels for advanced electric power plants, P. Dou, K. Yabuuchi

The ion irradiation damage of 3C-SiC, B. Li, K. Yabuuchi

International symposium of Biofunctional Chemistry: Towards the understanding of biological energy system, R. Sakaguchi, T. Morii

5. COLLABORATION WORKS IN THE LABORATORY FOR COMPLEX ENERGY PROCESSES

Collaboration Works in The Laboratory for Complex Energy Processes

1. Introduction

The laboratory was established for research on advanced energy by the collaborative projects among the researchers in the Institute of Advanced Energy to promote joint activity of our knowledge and wisdom to find solutions to these interdisciplinary energy/environmental problems. From such a viewpoint, the research targets of the laboratory are focused on two specific fields, (i) "advanced studies of science and technology on plasma energy and quantum energy" and (ii) "innovative studies of nano-bio functional materials for power generation". For this purpose, two sections (A2 and A3 mentioned below) are founded. In addition, A1 section promotes international or domestic collaborative research and assists activities such as academic meetings and seminars.

In order to pursue the above objectives of the Institute of Advanced Energy, it is essentially necessary to organize the cooperative research program with much closer connection between related research fields in the institute. The laboratory takes charge of organizing and promoting the cooperative research project as a center of research activity in the Institute. The research staffs in the institute participate in specific projects to carry out their subjects. The scientists of other faculties in Kyoto University can also participate in the cooperative project to enhance the progress of research and educational activities. The laboratory also manages various events such as symposium and seminar for related topics on energy field. The cooperative research activities will be published in a publication edited in the laboratory at the end of the fiscal year. Management of the technical staffs for large scale equipment are also under the responsibility of the laboratory.

A1 Division of International and Industrial Partnership

This division promotes international collaborative research on advanced energy to lead the field of energy science and technology as a worldwide pioneer. For this purpose, the symposium and the workshop organized by institution member are supported. This section also promotes young researcher/student exchange, coopera-

tive research activities and multi-lateral collaborative research with industries. Establishment of infrastructure and human resource development are also supported.

A2 Division of Plasma and Quantum Energy Research

This section promotes studies on advanced plasmas and quantum energy for realizing future energy systems, integrating plasma energy science and advanced energy material research. In particular, based on the results obtained in our related groups, we aim at extending the research fields and contributing to human society by utilizing the existing key devices such as Heliotron J, DuET, MUSTER and inertial electrostatic confinement (IEC) device, which have been developed in the institute.

A3 Division of Soft Energy Science Research

This division promotes studies on emergent materials and systems for realizing next generation soft energy system. In particular, functional nano- and bio-materials to efficiently utilize solar energy and bio-energy are studied by integrating laser science, nanotechnology, and bio-technology. We aim at extending our research fields by utilizing the existing devices such as System for Creation and Functional Analysis of Catalytic Materials, SEMs, SPM, Solar Simulator, KU-FEL and various laser systems.

2. The cooperative research program

A brief summary of the cooperative research subjects carried out in FY2019 are shown next pages, which were proposed by researchers of IAE and selected by the program committee of the Laboratory.

The framework of the cooperative researches in the section A2 and A3 have been changed last year. The financial resource is focused to a small number of project proposals under the leadership of the chairs of three divisions who review the proposals from IAE researchers and arrange the accepted ones.

As a result, the research themes of 10 were applied and applications of 10 were accepted. The number of research subjects is listed in Table 1 according to the project categories.

Table 1 Number of the accepted research subjects according to the standard project theme
The whole sum 5

Category			Total
A1	A2	A3	
6	2	2	10

The individual research subjects are as follows

A1

“Supporting Activities on International and Industrial Collaborative Research”

“**Organization of the third research seminar on RNA, and presentation and exchange of information in the seminar**”

- M. Katahira, T. Nagata, N. Hamad (Inst. Adv. Energy, Kyoto Univ.)
- A. Takeuchi (Graduate School of Medicine and Faculty of Medicine Kyoto Univ.)
- T. Shiina (Yukawa Institute for Theoretical Physics)
- R. Kurokawa, R. Yoneda (Saitama Med. Univ.)
- K. Mitsuoka (Osaka Univ.)
- T. Yamashita (Tokyo Univ.)
- S. Ishigaki (Nagoya Univ.)
- T. Oyoshi (Shizuoka Univ.)
- Y. Matsuno, N. Fukuda (Niigata Univ.)
- M. Ikeda, K. Hitachi (Fujita)
- Y. Ohishi (Japan Med. Univ.)

“**Workshop on Physics validation and control of turbulent transport and MHD in fusion plasma**”

- Y. Kishimoto, S. Ohshima (Inst. Adv. Energy, Kyoto Univ.)
- H. Tanaka, K. Imadera (Inst. Adv. Energy, Kyoto Univ.)
- A. Brerwage (QST)
- H. Park (Ulsan National Institute of Science and Technology)
- W. Lee, H. Jhng(NFRI)

“**Preparation of collaborative research agreement between United States- Japan universities centered on the university startup in New York City**”

- T. Hara, Y. Takatsuka (Inst. Adv. Energy, Kyoto Univ.)
- B. Sambrotto (Columbia Univ.)

“**The 32nd exchange meeting between industry and academia at Uji campus, Kyoto Univ.**”

- T. Hinoki, T. Nagata, K. Mukai (Inst. Adv. Energy, Kyoto Univ.)

“**Support for the 1st topical workshop of the wate-no-kai of the Japanese Beam Physics Club**”

- H. Zen. (Inst. Adv. Energy, Kyoto Univ.)
- K. Sakagami (PSC, Tokyo Univ.)

- H. Harada, Y. Fuwa (Japan Atomic Energy Agency)
- N. Yamamoto, Y. Honda, D. Naitoh (High Energy Accelerator Research Organization)
- K. Suga, (Osaka Univ.)
- T. Shibuya (National Institute of Advanced Industrial Science and Technology)
- “NEA International Workshop on Structural Materials for Innovative Nuclear Systems (SMINS-5)”
- A. Kimura, T. Hinoki, K. Yabuuchi (Inst. Adv. Energy, Kyoto Univ.)

A2

“**Production of MeV-class electrons by stochastic Landau-acceleration using non-resonant microwaves and its application to novel plasma initiation**”

- S. Kobayashi, K. Nagasaki, H. Ohgaki, T. Kii, H. Zen, T. Minami, S. Kado, S. Ohshima, H. Okada, T. Mizuuchi, S. Konoshima (Inst. Adv. Energy, Kyoto Univ.)
- S. Torsten, H. Laqua (Max-Planck Institute for Plasma physics)
- M. Preynas (Ecole polytechnique federale de Lausanne)
- “**Influences of three dimensional magnetic field on a diverter plasma in a torus device**”
- S. Ohshima, T. Minami, S. Kado, S. Kobayashi, H. Okada, K. Nagasaki, T. Mizuuchi, S. Konoshima, (Inst. Adv. Energy, Kyoto Univ.)
- R. Matoike (Grad. Sch. Energy Sci., Kyoto Univ.)

A3

“**Development of time-resolved fluorescent polarization system for measuring kinetic process of recognition and/or reaction and its application**”

- E. Nakata, T. Morii, K. Matsuda (Inst. Adv. Energy, Kyoto Univ.)
- Z. Zhengxiao, S. Muroi (Grad. Sch. Energy Sci., Kyoto Univ.)

“**Clarifying the formation mechanism of hydrogen bubbles during photocatalysis through time-resolved optical measurements**”

- T. Nakashima, K. Ando, T. Nohira (Inst. Adv. Energy, Kyoto Univ.)

THE LABORATORY SEMINARS

Laboratory Seminars

The Laboratory promotes topical academic seminars in order to strengthen the research activities in each research section and to enhance the mutual cooperation among a lot of academic fields. The Laboratory also planned a symposium on April 3, 2020 for discussions of the cooperative research results in FY2019. The meeting was cancelled due to the outbreak of the coronavirus.

In FY2019 seminars were held with following themes.

1. Topical Seminars

(1) July, 5, 2019

Y. Katoh (Kato)

“Overview of DOE ATF Goals & SiC/SiC Program”

*Distinguished Research Staff Group Leader
-Nuclear Structural Materials
Oak Ridge National Laboratory*

(2) July 12, 2019

①

S. Zinkle

“Radiation Damage Mechanism in Nuclear Materials”

The University of Tennessee

②

A. Ryazanov

“High-energetic Particle Irradiation Response of Nuclear Structural Materials”

National Research Center, Kurchatov Institute

(3) July 26, 2019

H.J. Lee

“Theoretical and numerical analyses of the turbulence and the anomalous transport caused by the shear flow in the cross-field discharges”

*Division of Electrical and Electronics Engineering
Pusan National University*

(4) December 9, 2019

H.J. Lee

“Application of Low-Temperature Plasmas for Skin-Treatment and Stem Cell Proliferation”

*Division of Electrical and Electronics Engineering
Pusan National University*

2. Colloquium

(1) June 6, 2019

K. Shinokita

“Control of valley relaxation in atomically thin semiconductors”

Inst. Adv. Energy, Kyoto Univ.

(2) July 16, 2019

T. Nishihara

“Tailoring thermal radiation spectrum based on excitation physics”

Inst. Adv. Energy, Kyoto Univ.

(3) July 26, 2019

K. Mukai

“Analysis of light element materials using X-ray and neutron”

Inst. Adv. Energy, Kyoto Univ.

(4) August 9, 2019

T. Mashima

“Understanding of three-dimensional structure and action mechanism of functional nucleic acids”

Inst. Adv. Energy, Kyoto Univ.

(5) August 22, 2019

S. Kobayashi

“Stochastic Landau acceleration in magnetic confinement configuration”

Inst. Adv. Energy, Kyoto Univ.

(6) September 12, 2019

T. Hayashi

“Statistical thermodynamics on the biomolecular recognition, and its application to the drug-development research”

Inst. Adv. Energy, Kyoto Univ.

6. PROJECTS WITH OTHER UNIVERSITIES AND ORGANIZATIONS

NIFS Bilateral Collaboration Research Program on Heliotron J

Since FY2004, the Heliotron J group at IAE, Kyoto University has joined the Bilateral Collaboration Research Program by National Institute for Fusion Science (NIFS), an Inter-University Research Institute. This unique collaboration program promotes joint researches bilaterally between NIFS and research institutes or research centers of universities that have unique facilities for nuclear fusion research. Under this collaboration scheme, the facilities operated in the different universities are open to all fusion researchers just as joint-use facilities of NIFS.

The main objective of the research in our Heliotron J group under this joint research program is to investigate experimentally/theoretically the transport and stability of fusion plasma in advanced helical-field, and to improve the plasma performance through advanced helical-field control in Heliotron J. Picked up in FY2019 are the following seven key-topics; (1) transport study concerning field configuration control and relating plasma structure formation control, (2) control of plasma profile, plasma flows, plasma current for confinement improvement, (3) investigation of structure formation of plasma fluctuations in core and peripheral region, (4) understanding of MHD instabilities of energetic particle modes and its control, (5) enhancement of operation region of high density plasmas, (6) optimization of particle supply and heating scenario, (7) development of new technology in experiment and analysis.

Only some results from this collaboration in FY2019 are shortly reported below. Annual report for all of the collaboration subjects in this program will be published by NIFS.

Reformation of the electron internal transport barrier (eITB) with the appearance of a magnetic island [1]: When realizing future fusion reactors, their stationary burning must be maintained and the heat flux to the divertor must be reduced. This essentially requires a stationary internal transport barrier (ITB) plasma with a fast control system. However, the time scale for determining the position of the foot point of an ITB is not clearly understood even though its understanding is indispensable for fast profile control. In this study, the foot point of the eITB was observed to be reformed at the vicinity of a magnetic island when the island started to form. In addition, the enhanced confinement region was observed to expand during the eITB formation according to the radial movement of the magnetic island toward the outer region. Compared to the time scales of the local heat transport, the faster time scales of the movement of the eITB foot point immediately after island formation (~0.5 ms) suggest the importance of the magnetic island for

plasma profile control.

Radial electric field during the formation of the electron internal transport barrier (eITB) [2]: Radial electric field in plasmas in helical plasma confinement devices significantly contributes to the neo-classical transport. It is estimated using plasma flow velocity from the charge-exchange recombination spectroscopy (CX-RS) for Heliotron J plasmas. The radial electric field is investigated in NBI and/or ECH plasmas during eITB appearance. In an NBI plasma, negative radial electric field, this means “ion root”, is observed. This electric field is almost explained by the neo-classical theory. Superimposing ECH in a NBI plasma, the electron temperature is increased and the density in the core region is decreased, then, the eITB appears. In this region, the radial electric field becomes positive, “electron root”. The radial electric field in the core region changes from negative to positive during the formation of eITB.

Bumpiness dependence of electron confinement, and temperature and density distributions [3]: Magnetic field ripple in the toroidal direction (bumpiness) in Heliotron J magnetic configuration is one of key parameters to control neo-classical particle transport and high energy particle confinement. The global plasma confinement has been studied and its bumpiness dependence was clarified. For the next step, the electron temperature and density distributions, and kinetic stored energy are measured by using Thomson scatter measurement system to investigate electron confinement properties in ECH plasmas under the condition of 270 kW in injection power. The high- and the medium-bumpiness configurations are almost same for the stored energy, however, in the low bumpiness case, the stored energy is low. At the higher bumpiness case, the stored energy becomes lower than that in the low bumpiness case. The anomalous transport is planned to study, since it is significant in the peripheral region in the plasma.

References

- [1] N. Kenmochi, et al., “Reformation of the Electron Internal Transport Barrier with the Appearance of a Magnetic Island”, *Scientific Reports* 10 (2020) 5.
- [2] S. Kobayashi, et al., “Effect of Magnetic Configuration on Energy Confinement, Energetic Particle and Momentum Transport in NBI Plasmas of Heliotron J”, 22nd ISHW (23-27 Sep. 2019, Madison, USA).
- [3] K. Nagasaki, et al., “Response of Plasma Performance to Magnetic Configuration, Fueling, and Heating/Current Drive in Heliotron J”, 22nd ISHW (23-27 Sep. 2019, Madison, USA).

7. HOW TO GET TO THE IAE

