


2-4. Research Clusters

No.	Name	Project Title
2-4-1	Hiroki MATSUO IROAST	Ferroelectric Photovoltaics
2-4-2	Gaochuang CAI IROAST	Next-Generation Design of Structures
2-4-3	Mitsuhiro AIDA IROAST (-06/2022)/FAST (07/2022-)	Plant Stem Cells and Regeneration
2-4-4	Shinya HAYAMI FAST	Development of Nano and Supramolecular Materials
2-4-5	Sinichiro SAWA FAST	Plant Cell and Developmental Biology
2-4-6	Makoto TAKAFUJI FAST	Nano-Organics and Nano-Hybrids
2-4-7	Hamid HOSANO IINa	Nano-medicine and Drug Delivery System
2-4-8	Takuro NIIDOME FAST	Nano-medicine and Theranostics
2-4-9	Jun OTANI FAST	Multiscale Modeling of Soil and Rock Materials Using X-ray CT
2-4-10	Toshifumi MUKUNOKI FAST	Micro CT-based quantification of fibrosis and vascularization in pancreatic tumor
2-4-11	Toshifumi MUKUNOKI FAST	Quantification of Three Dimensional Vascular Network
2-4-12	Yoji MINE FAST	Advanced Structural Materials
2-4-13	Sadahiro TSUREKAWA FAST	Microstructure Analysis and Grain Boundary Engineering
2-4-14	Ichiro AKAI IINa	Structure and Dynamics of Materials Using Quantum Beams and Data-Driven Sciences
2-4-15	Tetsuya KIDA FAST	Nano-materials for Energy Applications and Environmental Protection

FAST : Faculty of Advanced Science and Technology

IINa : Institute of Industrial Nanomaterials

FY2022 IROAST Research Cluster Activities Report

No.4-1	Ferroelectric Photovoltaics			
Cluster Coordinator				
Name	Hiroki MATSUO	Title	Associate Professor	
Affiliation	IROAST			
E-mail	Email: matsuo_h@cs.kumamoto-u.ac.jp			
Research Field	Advanced materials			
Cluster Members				
Name	Affiliation/Title			
Yuji NOGUCHI	Kumamoto University / Professor			
Daisuke KOSUMI	Kumamoto University / Associate Professor			
Ho-Yong LEE	Ceracomp Co. Ltd. / Professor, President			
Moon-Chan KIM	Ceracomp Co. Ltd. / Researcher			

1. Research outline and its perspective

Ferroelectric materials with spontaneous polarization (P_s) exhibit a characteristic photovoltaic (PV) response that does not appear in the pn junctions of conventional semiconductors. High photovoltages, light-polarization-dependent photocurrents, and fast photoresponse are appealing features of the ferroelectric PV effect. However, since typical ferroelectric oxides have wide bandgap, a vanishingly small photoresponse under visible light has been an issue to be overcome. In this term, ferroelectric PV properties of 1% Mn-doped BaTiO_3 ($\text{BaTi}_{0.99}\text{Mn}_{0.01}\text{O}_3$, Mn- BaTiO_3) single crystals were investigated (Fig. 1). We found that the optimal control of valance state of Mn is effective in enhancing the PV response under visible light irradiation.

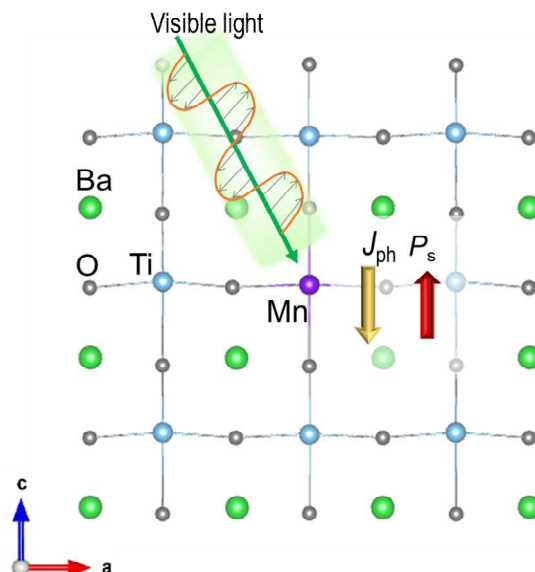


Fig. 1. Concept of this research. Mn atoms incorporated into crystal lattices of ferroelectric BaTiO_3 act as an active center for visible-light absorption generating photocurrents (J_{ph}).

2. Research progress and results

Ferroelectric and PV properties of Mn-BaTiO₃ single crystals grown by the solid-state crystal growth (SSCG) method were investigated. The growth of the single crystals was confirmed by X-ray diffraction measurements. A well-saturated polarization-electric field (E) hysteresis loop with a remanent polarization of 18 $\mu\text{C cm}^{-2}$ was obtained. Measurements of absorption spectrum for the single-crystal samples indicated that the absorption coefficient in the visible light region is enhanced by Mn doping.

To control the valence state of Mn to be Mn²⁺, Mn³⁺, Mn⁴⁺, and mixed state of Mn²⁺ + Mn³⁺, the single crystal samples were annealed at 900 °C under various partial oxygen pressures before the PV measurements. After a poling treatment to the annealed samples by the application of E in the $\langle 101 \rangle$, photocurrents flowing in the same direction were measured under light with various photon energy ($h\nu$). We found that the maximum photovoltage and photocurrent of were obtained for crystals with mixed valence state i.e., Mn²⁺ + Mn³⁺. Measurements of the $h\nu$ dependence of short-circuit photocurrents for the samples with the mixed valence state revealed that onset $h\nu$, where photocurrent starts to rise sharply, was around 1.6 eV, which was much lower than the bandgap energy of BaTiO₃ ($E_g = 3.2$ eV). Our density functional theory calculations indicate that the impurity levels derived from 3d orbitals of Mn²⁺ and Mn³⁺ are formed within the bandgap of BaTiO₃ as shown in Fig. 2. Moreover, the existence of long-lived excited state was suggested at probe energy lower than the bandgap energy. These experimental and calculation results indicate that impurity levels derived from Mn-3d orbitals promote the exciton generation probably by a two-step process leading to the enhanced PV response under visible light.

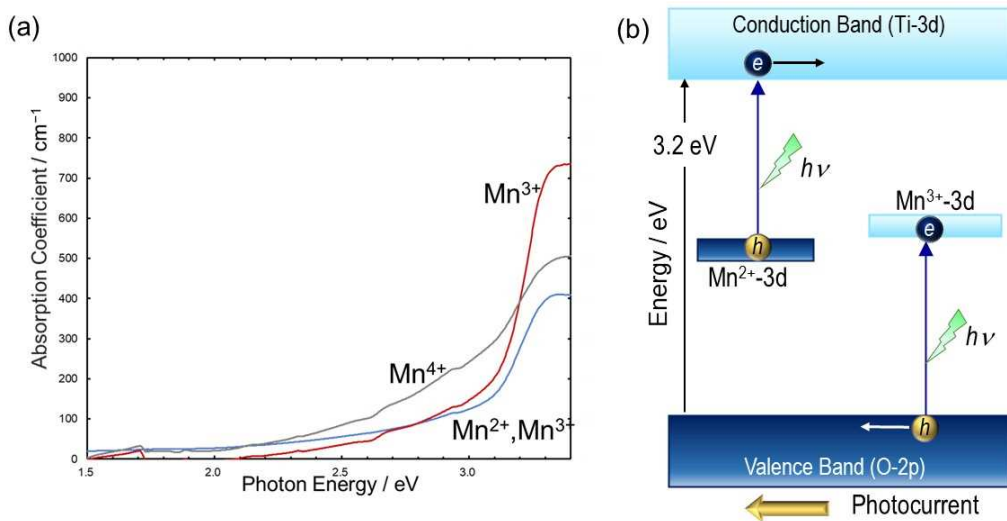


Fig. 2(a) Absorption spectra of Mn-BaTiO₃ single crystals with various valence states of Mn. (b) Schematic band diagram of Mn-BaTiO₃ with mixed valence state of Mn²⁺ and Mn³⁺.

3. Research plan for the next year

For further understating of the mechanisms of the enhanced PV response, transient absorption spectroscopy measurements for the samples with various valence states will be measured. Moreover, polarization dependence of photocurrents will be measured to clarify contributions of the bulk PV effect and domain-wall PV effect on the total PV response of Mn-BaTiO₃.

4. List of Grants

- 1) The Asahi Glass Foundation Research Encouragement Grants FY2022, 次世代蓄電デバイスに向けた新規欠陥双極子誘起強誘電体の創製, April 2022-March, 2023
- 2) Grant-in-Aid for Early-Career Scientists (The Japan Society for the Promotion of Science), April 2022-March 2023

5. Papers & Presentations


(Papers)

- 1) Hiroki Matsuo* and Yuji Noguchi
“High Photocurrent Anisotropy in Domain-Engineered Ferroelectrics for Visible - Light Polarization Detection”
Advanced Optical Materials 10(21) 2201280 (2022)
<https://doi.org/10.1002/adom.202201280>

(Presentations)

- 1) **(Invited)** Hiroki Matsuo*
The 77th Ceramic Society of Japan Awards for Advancements in Ceramic Science and Technology
“Development of Photovoltaic Functions in Perovskite-type Ferroelectric Materials”
Annual Meeting 2023 of the Ceramic Society of Japan, Mar. 2023, Yokohama.
- 2) Hiroki Matsuo and Yuji Noguchi
“Domain-engineered BiFeO₃-base ferroelectric with high-photocurrent anisotropy for visible-light polarization detection”
13th Korea-Japan Conference on Ferroelectrics (KJC-FE13), Sep. 2022, Busan (Virtual)
- 3) Hiroki Matsuo and Yuji Noguchi
“Ferroelectric Photovoltaic Effect in BiFeO₃-based solid-solution thin films with nanodomain structures”
35th Fall Meeting of the Ceramic Society of Japan, Sep. 2022, Tokushima (Virtual).
- 4) Hiroki Matsuo and Yuji Noguchi
“Enhanced photovoltaic effects in ferroelectric thin films with nanodomains”
15th International Symposium on Ferroic Domains & Micro- to Nano-scope Structures (ISFD-15), Aug. 2022, Yamanashi.

FY2022 IROAST Research Cluster Activities Report

No.4-2	Next-Generation Design of Structures			
Cluster Coordinator				
Name	Gaochuang CAI	Title	Associate professor	
Affiliation E-mail	IROAST Email: cai@kumamoto-u.ac.jp			
Research Field	Environment-friendly technology / Strengthening resilience / Advanced materials /			
Cluster Members				
Name	Affiliation/Title			
Kazuo DAN	Faculty of Advanced Science and Technology, Kumamoto University (KU) /Full professor			
Amir Si LARBI	University of Lyon, France/ Full professor			
Konstantinos Daniel TSAVDARIDIS	City, University of London, U.K./ Full professor			
Danièle WALDMANN	Insitut für Massivbau (Institute of Concrete and Masonry Structures), Technischen Universität Darmstadt, Germany/ Full professor			

[Details of activities]

1. Research outline and its perspective

The research unit aims to the two key research themes, i.e., (1) safety and optimization of structures under extreme loads (e.g. earthquake-fire, LPGM, NFGM) including the application of high-performance materials, and (2) recycling of wastes arising from the extreme loads, in particular the application in the concrete industry, and strengthening the well-designed structures with limited damages subjected to the extreme loads. The two themes also can be shortly called *Design for structural safety and sustainability* (DfS³), one of the most important parts of Design for X (DfX).

Since December 2021, the research activities will be conducted using advanced numerical methods, algebraic analysis, and experimental verification. As the PI of the unit, the applicant has rich experience in collaboration with international leading academic partners and local industry partners.

2. Research progress and results in the fiscal year (attach 1-2 related photos)

Regarding the seismic safety of building structures with resilient RC elements, since the structural laboratory at Kumamoto University has not been used for the past ten years, a lot of finishing equipment will be required from October 2021, and the first phase experiments have been conducted in September 2022. Our focuses are to experimentally investigate the seismic behavior and to propose the design method of RRC elements under strong earthquakes. The test data is being analyzed now.

About the wall-precast concrete (WPC) systems which significantly consider the safety and sustainability of the structures, even located in earthquake-prone areas, we have experimentally

investigated the seismic behavior of the shear walls in the WPC system, and developed high accuracy FE analysis method to evaluate the seismic performance. The concept and FE model and verification are shown in Figs.1 and 2.

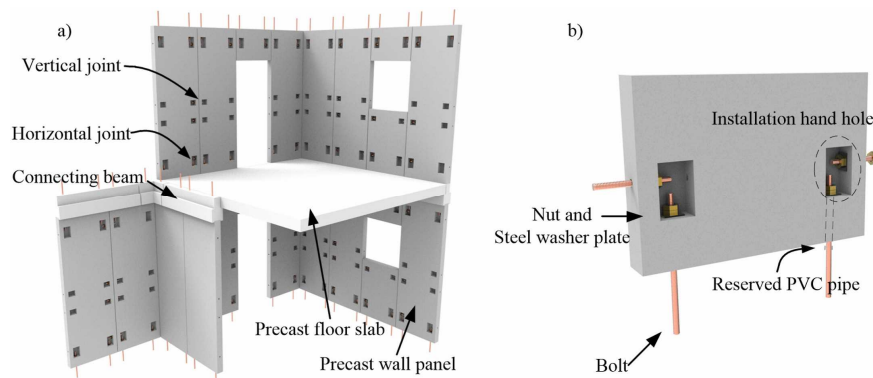


Fig.1 WPC house concept

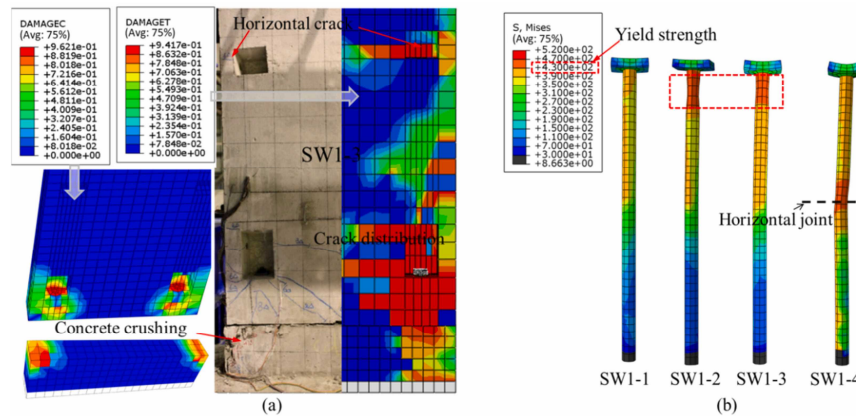


Fig. 2 Comparison of FEA results: (a) concrete damage, (b) stress distribution of steel bolts.

3. Research plan for the next year

According to the current process and results, the following research projects will be conducted next year,

- (1) Seismic performance and FE analysis of Resilient RC (RRC) shear walls under strong earthquake
- (2) Seismic performance and FE analysis of RRC columns under strong earthquake
- (3) Seismic performance and FE analysis of FRP-repaired RRC columns under strong earthquake
- (4) Seismic performance and FE analysis of Steel-RC (SRC) columns under strong earthquake
- (5) Structural performance and FE analysis of RRC beams under impact loads

These projects will be conducted by two researchers, 4 Ph.D. students, and two Master students at Kumamoto University. Based on the projects, more than 6 journal articles will be submitted.

4. List of awards, grants, and patents.

-Grants

Seismic Performance and AI-based Evaluation Method of SRC Rectangular Columns Subjected to Multiple Repeated Cyclic Loads


Research Grant Ohata Foundation, 2,000,000JPY, 2022.10-2023.9

5. List of journal papers (with IROAST as your affiliation) published between April 2022 and

March 2023

- [1] Su, Q., **Cai, G.***, Hani, M., **Si Larbi, A.**, & **Tsavidaridis, K. D.** (2023). Damage control of the masonry infills in RC frames under cyclic loads: a full-scale test study and numerical analyses. *Bulletin of Earthquake Engineering*, 21(2), 1017-1045. (IF:4.556, Q1)
- [2] Wang, Y., & **Cai, G.*** (2023). Seismic behavior of square concrete columns confined by FRP-steel composite tube. *Journal of Building Engineering*, 65, 105754. (IF:7.144, Q1)
*Issued on April 15, 2023
- [3] Zhao, F., Xiong, F., **Cai, G.***, Yan, H., Liu, Y., & **Si Larbi, A.** (2023). Performance and numerical modelling of full-scale demountable bolted PC wall panels subjected to cyclic loading. *Journal of Building Engineering*, 63, 105556. (IF:7.144, Q1)
- [4] Chen, G., Wang, Y., **Cai, G.***, **Si Larbi, A.**, Wan, B., & Hao, Q. (2022). Performance and modeling of FRP-steel dually confined reinforced concrete under cyclic axial loading. *Composite Structures*, 300, 116076. (IF:6.603, Q1)

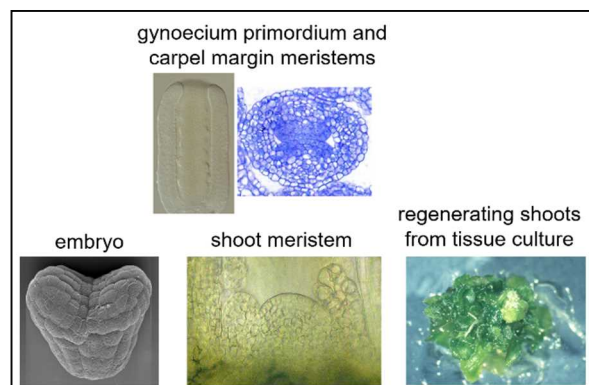
FY2022 IROAST Research Cluster Activities Report

No.4-3	Plant Stem Cells and Regeneration			
Cluster Coordinator				
Name	Mitsuhiro AIDA	Title	Professor	
Affiliation E-mail	Faculty of Advanced Science and Technology (FAST) E-mail : m-aida@kumamoto-u.ac.jp			
Research Field	Environmental bioscience			
Cluster Members				
Name	Affiliation/Title			
Yoshihisa IKEDA	Centre of the Region Haná for Biotechnological and Agricultural Research, Czech Advanced Technology and Research Institute (CATRIN), Palacký University/Junior Researcher			
Stefan de FOLTER	Unidad de Genómica Avanzada (LANGEBIO), Centro de Investigación y de Estudios Avanzados del Instituto Politécnico Nacional (CINVESTAV-IPN), Guanajuato, México			
Jose Irepan Reyes-O LALDE	Universidad Estatal del Valle de Toluca, Ocoyoacac Edo. Mex. Mexico			

[Details of activities]

1. Research outline and its perspective

Plants have remarkable ability of regeneration, enabling single differentiated cells to be reprogrammed their fates and developed into a whole plant. This process involves de novo formation of stem cell tissue called the meristem and relies on the actions of two plant hormones, cytokinin and auxin. In this research cluster, we explore regulatory mechanisms of gene cascade dictated by a set of transcription factors involved in tissue regeneration.

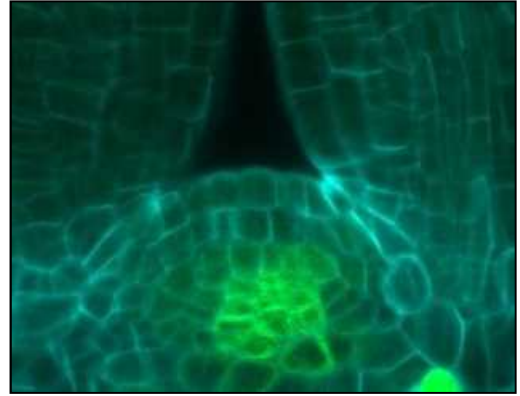


Related developmental processes such as embryogenesis and gynoecium development will also be studied.

2. Research progress and results in the fiscal year

Embryonic shoot meristem formation is a process that establishes a stem cell population responsible for producing the whole shoot system of a plant. It is known that the mechanisms regulating this process involve common factors that are responsible for shoot regeneration. For example, a common set of transcription factors including WUS, STM and CUC proteins are required for shoot meristem formation both in embryogenesis and regeneration. Also, high cytokinin to auxin ratio conditions shoot formation in both developmental contexts. This year, we examined how the pattern of cytokinin response develops during embryonic shoot meristem formation by using a reporter gene that monitors transcriptional response to cytokinin. The results showed that the low level of response was initiated in inner cells at the

globular stage in a region that gives rise to the shoot meristem, and it gradually extended towards the protodermal layer by the torpedo stage. At the bending-cotyledon stage where morphological features of the shoot meristem became evident, cytokinin response was repressed in the outer two cell layers that include protodermal cells, resembling that observed in the postembryonic shoot meristem. These results suggest that establishment of cytokinin response distribution occurs gradually and is under complex regulation. The cytokinin response in the presumptive shoot meristem was dependent on the activities of the CUC proteins, which are essential regulators required for shoot meristem formation. Our results thus identify key factors for establishing cytokinin response during embryonic shoot meristem formation.



3. Research plan for the next year

Establishment of the region with high cytokinin response is an important process for the formation of shoot meristems in various developmental contexts. In the next year, we will focus on the gynoecium, which is a female reproductive structure in angiosperms. Gynoecium primordium is initiated from the floral meristem, a modified form of the shoot meristem and in turn, the primordium initiates another type of meristematic tissue called carpel margin meristems, which are responsible for producing internal organs of the gynoecium such as ovules and septa. It has been already known that the CUC transcription factors play an important role in promoting the activity of carpel margin meristems partly through activating the expression of another shoot meristem specific transcription factor STM. It is also known that high cytokinin response is associated with carpel margin meristems. By using reporter genes, we will analyze precise spatiotemporal patterns of CUC, STM, and cytokinin response. Genetic analyses will also be carried out to investigate relationship among these factors. In addition, pharmacological experiments will be performed to examine whether the CUC and STM proteins are involved in cytokinin signaling. These experiments will shed light on the molecular mechanisms involved in the establishment of the meristematic tissue required for gynoecium formation.


4. List of awards, grants, and patents, if any.

N/A

5. List of journal papers

N/A

FY2022 IROAST Research Cluster Activities Report

No.4-4	Development of Nano and Supramolecular Materials			
Cluster Coordinator				
Name	Shinya HAYAMI	Title	Professor	
Affiliation	Faculty of Advanced Science and Technology (FAST)			
E-mail	E-mail : hayami@kumamoto-u.ac.jp			
Research Field	Biotechnology & healthcare technology / Environmental bioscience / Environment-friendly technology / Advanced materials			
Cluster Members				
Name	Affiliation/Title			
Shintaro IDA	Kumamoto University / Professor			
Yoshihiro SEKINE	Kumamoto University / Associate Professor			
Zhongyue ZHANG	Kumamoto University / Associate Professor			
Michio KOINUMA	Kumamoto University / Associate Professor			
Jorge BELTRAMINI	Queensland University of Technology / Professor, IROAST Visiting Professor			
Yang KIM	Kosin University / Professor, IROAST Visiting Professor			
Martino DI SERIO	University of Naples Federico II / Professor, IROAST Visiting Professor			
Shie-Ming PENG	National Taiwan University, IROAST Visiting Professor			
Parasuraman SELVAM	Indian Institute of Technology-Madras, IROAST Visiting Professor			

[Details of activities]

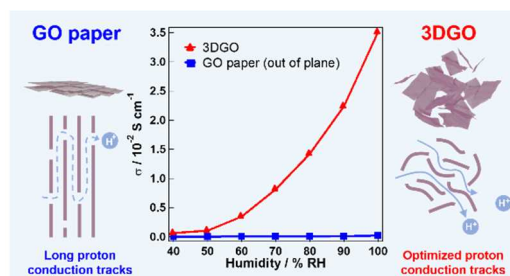
1. Research outline and its perspective

Graphene oxide (GO) has been considered as only a precursor for graphene but also one of the most promising materials because of its excellent properties such as photoluminescence, ferromagnetism, electrodes, and water permeation. As it is now, it is said that GO has wider range of applications than graphene. Therefore, it is important for industrial development to study GO. Recently, we focused on (i) ion conduction for fuel cell, (ii) biomass conversion reaction, (iii) agri-bio application by using GO nanosheet and its derivatives.

2. Research progress and results in the fiscal year

(i) Upswing in fuel cell performance using ultra fast out-of-plane proton conducting three-dimensional graphene oxide as electrolyte

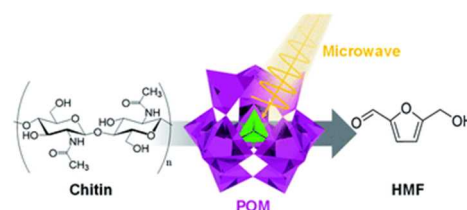
Despite the considerable in-plane proton conductivity of graphene oxide (GO) nanosheets, the inadequate single cell performance in polymer exchange membrane fuel cell (PEMFC) was observed by incorporating vacuum filtration induced GO membrane between the electrodes. Particularly, the proton transfer direction between the electrodes in the PEMFC single cell is in the out-of-plane of GO membrane which is significantly lower than the in-plane direction due to the barriers of the proton conduction pathway by turbostratic stacking of GO layers. Therefore, the structural transformations of GO nanosheets towards ultra-fast out-of-plane proton conduction are the key to boost the performance of GO-based PEMFC. Here, we report the freeze-dried route driven three-dimensional graphene oxide



(3DGO) that exhibited a 3D interconnected network and significant interlayer void space. The out-of-plane direction proton conductivity of 3DGO is calculated as $3.5 \times 10^{-2} \text{ S cm}^{-1}$ at 343 K and 100 % relative humidity (RH) which is about 175 times higher proton conductivity than GO membrane. The 3DGO was incorporated as a solid electrolyte in PEMFC single cell and the maximum power density of 60.2 mWcm^{-2} has been obtained at $30 \text{ }^\circ\text{C}$ which is the highest record value among pure GO fuel cells. Moreover, the high open-circuit voltage (OCV) of 1.02 V indicates the suitability of practical use and low fuel crossover in the system. This high proton conductivity and PEMFC performance of 3DGO could be correlated with the facile proton conduction pathway and higher water molecules uptake in the 3D porous architecture of 3DGO.

(ii) Microwave-assisted catalytic conversion of chitin to 5-hydroxymethylfurfural using polyoxometalate as catalyst

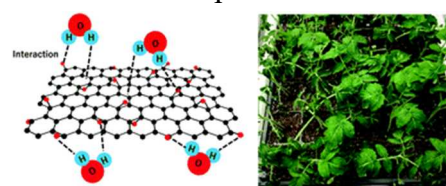
The key challenges for converting chitin to 5-hydroxymethylfurfural (5-HMF) include the low 5-HMF yield. Moreover, the disadvantages of traditional acid–base catalysts including complex post-treatment processes, the production of by-products, and severe equipment corrosion also largely limit the large-scale conversion of chitin to 5-HMF. In this view, herein we have demonstrated a microwave aided efficient and green conversion of chitin to 5-HMF while using polyoxometalate (POM) as a catalyst and DMSO/water as solvent. Chitin treated with H_2SO_4 followed by ball-milling (chitin- H_2SO_4 -BM) was selected as the starting compound for the conversion process. Four different POMs including $\text{H}_3[\text{PW}_{12}\text{O}_{40}]$, $\text{H}_3[\text{PMo}_{12}\text{O}_{40}]$, $\text{H}_4[\text{SiW}_{12}\text{O}_{40}]$ and $\text{H}_4[\text{SiMo}_{12}\text{O}_{40}]$ were used as catalysts. Various reaction parameters including reaction temperature, amount of catalyst, mass ratios of water/DMSO and reaction time have been investigated to optimize the 5-HMF conversion.



The $\text{H}_4[\text{SiW}_{12}\text{O}_{40}]$ catalyst exhibited the highest catalytic performance with 23.1% HMF yield at optimum operating conditions which is the highest among the literature for converting chitin to 5-HMF. Significantly, the disadvantages of the state of the art conversion routes described earlier can be overcome using POM-based catalysts, which makes the process more attractive to meet the ever-increasing energy demands, in addition to helping consume crustacean waste.

(iii) High water adsorption features of graphene oxide: potential of graphene oxide-based desert plantation

we have demonstrated the effect of GO in the hydration of soil for tomato plantations. The soil that contains GO showed a better growth of tomato plants compared to that of bare soil, which might be attributed to the water adsorption ability of GO. The oxygenated functional groups of GO facilitated the adsorption of water in the soil, thereby improving the overall water adsorption of the soil. The results from the current findings can be a future guide for GO-assisted plantation in low water supply areas and/or desert plantations. Moreover, the outcome might be applied for the cultivation of other plants while GO can be utilized for better hydration of the soil.



3. Research plan for the next year

The future growth of carbon-based materials towards the goal of large-scale commercialization of the technologies largely depends on the better understanding and the subsequent control on the carbon substrate. The fabrication of ideal nano-architecture with appropriate surface texture (size, shape, porosity) and low cost are the primary concern to achieve the maximum performance from the energy conversion and storage device. In the case of electrode support materials for PEMFCs and SCs electrodes, the suitable structures and morphologies of the materials can promote the exposure of active sites to increase the catalytic activity/charge storage and enhance long-term stability. The possible new directions to prepare advanced nano-structure from carbon allotropes

include the fabrication of a unique 3D network with interconnected pores from the blending of 0D CQDs, 1D CNTs and 2D graphene sheets. The well-fitted compositions with a homogeneous mix-up of components allow unique synergistic effects, in which each unit exerts its own advantages and overcomes the deficiencies of the other units. In addition, the introduction of heteroatoms is capable of increasing the active sites, molecular structure, bandgap and charge mobility. Thus, the materials have a strong influence on the performance.

On the other hand, graphene oxide (GO), one of the nanomaterials, is a nanosheet material with many oxygen functional groups. Its high water content and ability to supply water and adsorb salts prevents salt damage and makes it possible to promote plant growth and forest improvement using GO soil. The large number of oxygen functional groups enables effective decomposition and conversion of biomass through strong interactions such as hydrogen bonding and oxidizing power. We will conduct mass synthesis of graphene oxide (GO) nanosheet materials suitable for each application, and promote demonstration experiments for CO₂ reduction and biomass supply, such as promotion of plant growth in barren areas and forest improvement in GO soils, and develop highly efficient, highly selective, and innovative biosynthesis of GO and GO hybrids from agricultural and wood wastes and other biomass. The project targets the development of biofuels through innovative biomass decomposition and conversion reactions with high efficiency and high selectivity, using GO as a base and catalyst material, and developing biofuels with high efficiency and high yield based on the promotion of plant growth and forest improvement in GO soil and the decomposition and conversion of biomass with GO in a water-soluble, one-pot reaction. Development of biofuels with high efficiency and high yield based on the decomposition and conversion of biomass by water-soluble and one-pot reactions with GO. Furthermore, by mixing GO with seawater, we aim to establish a social infrastructure for recycling systems based on the SDGs, such as CO₂ reduction, by realizing desalination from seawater for agricultural use with a simple method.

4. List of awards, grants, and patents, if any.


KAKENHI, Grant-in-Aid for Challenging Research (Exploratory) 2022-2023

5. List of journal papers published between April 2022 and March 2023

1. S. Kusumoto, A. Atoini, S. Masuda, Y. Koide, J. Y. Kim, S. Hayami, Y. Kim, J. Harrowfield, P. Thuery, Flexible Aliphatic Diammonioacetates as Zwitterionic Ligands in UO₂²⁺ Complexes: Diverse Topologies and Interpenetrated Structures, *Inorg. Chem.*, 2023.
2. S. Kusumoto, R. Suzuki, M. Tachibana, Y. Sekine, Y. Kim, S. Hayami, Recrystallization solvent dependent elastic/plastic flexibility of an n-dodecyl-substituted tetrachlorophthalimide,
3. Y. Sekine, S. Kusumoto, A. Sugimoto, M. Nakaya, S. Hayami, Crystal Design for Tuning the Mechanical Flexibilities of M(salophen) Complexes, *Cryst. Growth Des.*, 23, 2013–2017(2023) Cover Picture
4. K. J. Howard-Smith, A. R. Craze, R. Tokunaga, T. Taira, H. Min, M. J. Wallis, D. J. Fanna, S. Hayami, F. Li, High-Temperature Spin Crossover in Fe^{III} N₄O₂ Complexes Incorporating an [R-sal₂323] Backbone, *Cryst. Growth Des.*, 2023
5. M. A. Rahman, J. Yagy, Md. S. Islam, M. Fukuda, S. Wakamatsu, R. Tagawa, Z. Feng, Y. Sekine, J. Ohya, S. Hayami, Three-Dimensional Sulfonated Graphene Oxide Proton Exchange Membranes for Fuel Cells, *ACS Appl. Nano Mater.*, 2023.
6. N. N. Rabin, Md. S. Islam, M. A. Rahman, R. Tagawa, Y. Shudo, Y. Sekine, S. Hayami, Free-standing graphene oxide/oxidized carbon nanotube films with mixed proton and electron conductor properties, *Energy Adv.*, 2, 293-297(2023)
7. S. Kusumoto, Y. Kim, S. Hayami, Flexible metal complex crystals in response to external mechanical stimuli, *Coord. Chem. Rev.*, 475, 214890(2023).
8. S. Kusumoto, Y. Atoini, S. Masuda, J. Y. Kim, S. Hayami, Y. Kim, J. Harrowfield, P. Thuery, Zwitterionic and Anionic Polycarboxylates as Coligands in Uranyl Ion Complexes, and Their

- Influence on Periodicity and Topology, *Inorg. Chem.*, 61(38), 15182-15203(2022).
9. M. J. Wallis, A. R. Craze, H. Zenno, R. Tokunaga, T. Taira, H. Min., M. M. Bhadbhade, S. K. Bhattacharyya, R. Tian, A. Rich, S. Hayami, J. K. Clegg, C. E. Marjo, L. F. Lindoy, F. Li, Unique Spin Crossover Pathways Differentiated by Scan Rate in a New Dinuclear Fe(II) Triple Helicate: Mechanistic Deductions Enabled by Synchrotron Radiation Studies, *ChemRxiv.*, (2022).
 10. H. Min, A. R. Craze, M. J. Wallis, R. Tokunaga, T. Taira, Y. Hirai, M. M. Bhadbhade, D. J. Fanna, C. E. Marjo, S. Hayami, L. F. Lindoy, F. Li, Spin Crossover Induced By Changing the Identity Of the Secondary Metal Species In A Face-Centred FeII8NiIII6 Cubic Cage, *ChemRxiv.*, (2022).
 11. I. Ullah, J. W. Shin, R. Tokunaga, S. Hayami, H. J. Shin, K. S. Min, Anion-Dependent Cu(II) Coordination Polymers: Geometric, Magnetic and Luminescent Properties, *Crystal.*, 12(8), 1096 (2022).
 12. Y. Sekine, R. Akiyoshi, S. Hayami, Recent advances in ferroelectric metal complexes, *Coord. Chem. Rev.*, 469, 214663(2022).
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 14. M. A. Rahman, N. N. Rabin, Md. S. Islam, M. Fukuda, J. Yagy, Z. Feng, Y. Sekine, L. F. Lindoy, J. Ohyama, S. Hayami, Synergistic Strengthening in Graphene Oxide and Oxidized Single-walled Carbon Nanotube Hybrid Material for use as Electrolytes in Proton Exchange Membrane Fuel Cells, *Chem. Asian J.*, e202200376 (2022).
 15. T. Nakano, T. Abe, T. Matsumoto, K. Nakamura, S. Hayami, Y. Shiota, K. Yoshizawa, S. Ogo, Light-driven oxidation of CH₄ to C₁ chemicals catalysed by an organometallic Ru complex with O₂, *RSC Adv.*, 12(20), 12253-12257 (2022).
 16. S. Kusumoto, Y. Atoini, S. Masuda, Y. Koide, J. Y. Kim, S. Hayami, Y. Kim, J. Harrowfield, P. Thuery, Varied role of organic carboxylate dizwitterions and anionic donors in mixed-ligand uranyl ion coordination polymers *CrystEngComm.*, 24(44), 7833-7844(2022).
 17. A. Sugimoto, S. Kusumoto, M. Nakaya, Y. Sekine, L. F. Lindoy, S. Hayami, Modulation of the elasticity of single crystal, 1-D metal dimethylglyoximate complexes via solid solution effect, *CrystEngComm.*, 24(26), 4656-4660(2022). Inside Front Cover
 18. H. J. Shin, Y. J. Jang, H. Zenno, S. Hayami, K. S. Min, Formation of polynuclear iron(III) complexes of N-(2-pyridylmethyl)iminodipropanol depending on pseudohalide ions: synthesis, crystal structure, and magnetic properties, *J. Ind. Eng. Chem.*, 110, 345-356 (2022).
 19. J. Yagy, Md. S. Islam, H. Yasutake, H. Hirayama, H. Zenno, A. Sugimoto, S. Takagi, Y. Sekine, S. Ohira, S. Hayami, Insights and Further Understanding of Radioactive Cesium Removal Using Zeolite, Prussian Blue and Graphene Oxide as Adsorbents, *Bull. Chem. Soc. Jpn.*, 95, 862-870(2022).
 20. J. W. Shin, I. Ullah, R. Tokunaga, S. Hayami, K. S. Min, Air oxidation-induced single-crystal-to-single-crystal transformation of a mixed-valence tetranuclear Fe(II)-Fe(III) complex, *Dalton Trans.*, 51(38), 14429-14433 (2022).
 21. S. Jiajaroen, W. Dungkeaw, F. Kielar, M. Sukwattanasinitt, S. Sahasithiwat, H. Zenno, S. Hayami, M. Azam, S. I. Al-Resayes, K. Chainok, Four series of lanthanide coordination polymers based on the tetrabromobenzene-1,4-dicarboxylate ligand: structural diversity and multifunctional properties, *Dalton Trans.*, 51(19), 7420-7435 (2022).
 22. R. Akiyoshi, S. Hayami, Ferroelectric coordination metal complexes based on structural and electron dynamics, *Chem. Commun.*, 58(60), 8309-8321(2022).

FY2022 IROAST Research Cluster Activities Report

No.4-5	Plant Cell and Developmental Biology			
Cluster Coordinator				
Name	Sinichiro SAWA	Title	Professor	
Affiliation E-mail	Faculty of Advanced Science and Technology (FAST)/ International Research Center for Agricultural and Environmental Biology (IRCAEB) Email: sawa@kumamoto-u.ac.jp			
Research Field	Environmental bioscience			
Cluster Members				
Name	Affiliation/Title			
Carolina ESCOBAR	Professor, University of Castilla La Mancha Spain			
Bruno FAVERY	INRAE senior scientist (DR2), CNRS Institut Sophia Agrobiotech France			
Mitsuhiro AIDA	GSST Professor			
Takumi HIGAKI	GSST Professor			
Yuki YOSHIDA	FAST Project Assistant Professor			
Hidehiko SUNOHARA	FAST Visiting Assistant Professor			
Reira Suzuki	FAST Visiting Assistant Professor			

[Details of activities]

1. Research outline and its perspective

In this Research Unit, Plant Cell and Developmental Biology, we characterize the molecular and physical mechanisms that contribute to plant development and plant–parasitic nematodes interactions using genetic, biochemical, physiological approaches.

2. Research progress and results in the fiscal year

Meloidogyne incognita is one of the most detrimental root-knot nematode pests in the world, infecting almost all plant species. In this year, we have identified that local auxin synthesis mediated by YUCCA4 induced during RKN infection positively regulates gall growth and nematode development. Further, we have found that Rhamnogalacturonan-I functions as a nematode chemoattractant from Lotus corniculatus L. Supergrowing root culture.

We have also developed a new rapid method for detection of the root-knot nematode resistance gene, Mi-1.2, in tomato cultivars.

In order to discuss widely about our activities, we had an international meeting in Kumamoto, “plant development and biotic interaction” on December 13 and attended by about 60 faculty and students including IROAST director, Kazuki Takashima (left photo) and Bruno Favery (right photo) and his team members. After opening remarks and an introduction of overview of Kumamoto University and IROAST by Director Takashima, researchers from France and within the university gave presentations and engaged in discussions.

During the lunch break, graduate students from Kumamoto University gave poster presentations. Students received advice from overseas researchers and exchanged opinions about their research in relaxed settings, offering a good experience for the students.



3. Research plan for the next year

We will continue collaboration about plant development and biotic interaction.

4. List of awards, grants, and patents, if any.

Principal Investigator

1. Kakenhi, Grant-in-Aid for Young Scientists (A)
2. Kakenhi, Grant-in-Aid for Exploratory Research
3. JSPS, Bilateral program for joint research project
4. JSPS, Fostering Joint International Research (B)
5. Research grant from The Yanmar Environmental Sustainability Support Association

Co-PI

1. Kakenhi, Grant-in-Aid for Scientific Research on Innovative Areas (PI; Taku Demura, NAIST)
2. Kakenhi, Grant-in-Aid for Young Scientists (B) (PI; Akira Yamawo, Hirosaki Univ.)
3. JSPS, Bilateral Programs, Joint Research Projects (PI; Yasuhiro Kadota, Riken)
4. AMED, 21ak0101158h0001 (PI; Shogo Misumi)

5. List of journal papers (with IROAST as your affiliation) published between April 2022 and March 2023


Nakagami, S., Aoyama, T., Sato, Y., Kajiwara, T., Ishida, T., and Sawa, S. (2023) CLE3 and its homologues share overlapping functions in the modulation of lateral root formation through CLV1

and BAM1 in *Arabidopsis thaliana*. *Plant J.* 113. 1176-1191. doi.org/10.1111/tpj.16103

Oota, M., Toyoda, S., Kotake, T., Wada, N., Hashiguchi, M., Akashi, R., Ishikawa, H., Favery, B., Tsai, A., Yi-Lun, and Sawa, S. Rhamnogalacturonan-I as a nematode chemoattractant from *Lotus corniculatus* L. Supergrowing Root culture. *Frontiers in Plant Science*, 13:1008725, 2022. <https://doi.org/10.3389/fpls.2022.1008725>

Suzuki, R., Kanno, Y., Abril-Urias, P, Seo, M., Escobar, C., Tsai, A., Yi-Lun, and Sawa, S. Local Auxin Synthesis Mediated by YUCCA4 Induced during Root-knot Nematode Infection Positively Regulates Gall Growth and Nematode Development. *Frontiers in Plant Science*, 13:1019427, 2022. <https://doi.org/10.3389/fpls.2022.1019427>

FY2022 IROAST Research Cluster Activities Report

No.4-6	Nano-Organics and Nano-Hybrids			
Cluster Coordinator				
Name	Makoto TAKAFUJI	Title	Professor	
Affiliation E-mail	Faculty of Advanced Science and Technology (FAST) Email: takafuji@kumamoto-u.ac.jp			
Research Field	Advanced materials			
Cluster Members				
Name	Affiliation/Title			
Yutaka KUWAHARA	Faculty of Advanced Science and Technology (FAST) Kumamoto University Assistant Professor			
Hirotsuka IHARA	Faculty of Advanced Science and Technology (FAST) Kumamoto University Professor Emeritus			
Nanami HANO	Faculty of Advanced Science and Technology (FAST) Kumamoto University Université de Bordeaux, France JSPS Overseas Research Fellow			
Reiko ODA	CNRS, Université de Bordeaux, France Research Director <i>IROAST Visiting Professor</i>			
Josep-Lluís BARONA-VILAR	Instituto de Historia de la Medicina y de la Ciencia López Piñero (IHMC), Universidad de Valencia, Spain Professor <i>IROAST Visiting Professor</i>			
Zhenghe XU	College of Engineering, Southern University of Science and Technology, China Dean Department of Chemical and Materials Engineering, University of Alberta, Canada Teck Professor <i>IROAST Visiting Professor</i>			
Etsuko FUJITA	Chemistry Division, Brookhaven National Laboratory, USA Senior Scientist Emeritus <i>IROAST Visiting Professor</i>			

[Details of activities]

1. Research outline and its perspective

Our research cluster named “Nano-Organics and Nano-Hybrids” at the IROAST focuses on functional nano-objects composed of organics, inorganics and hybrids. Eight members including four visiting professors of IROAST from France, Spain, United States and China join the research cluster. The international collaborative projects regarding basic and advanced chemistry on nano-organics and nano-hybrids are initiated and carried out by each member, and their targets are widely distributed across highly diverse fields.



Excursion after the 13th IROAST Symposium (Japan-France Joint Seminar), in November 2022.

2. Research progress and results in the fiscal year

2-1. Exchanges of members regarding with international collaboration

We could meet and have fruitful discussion for recent results and future research tasks with the following collaborators:

University of Bordeaux (UB), France

The second term of the joint research project, the Laboratoire international associé (LIA) - 'Chiral nanostructures for photonic applications' (CNPA), of the University of Bordeaux (UB) with Kumamoto University (KU) and Kyoto University since 2015, is proceeding. The project has been approved by the Agence Nationale de la Recherche (ANR), France. Dr. Oda (Visiting Professor of IROAST) and Prof. Ihara are co-PIs on the Japanese and French sides, respectively, and Prof. M. Takafuji and Dr. Kuwahara are associated as core members. In 2022, total three Japanese member visited to UB in Sep. 2022 and Feb. 2023. Also, seven French members including Dr. R. Oda visited to KU and joined in the 13th IROAST Symposium organized by this cluster members on November 9, 2022.

Dr. Nanami Hano, a member of the research unit “Nano-organics and Nano-hybrids”, has joined R. Oda’s group as a JSPS Overseas Research Fellow from March, 2022. She will accommodate in UB for two years and may accelerate our collaborations.



Visit of French researchers and Dr. Oda to Kumamoto University in November, 2022

(Meeting with Prof. Takashima, IROAST Director)



The 13th IROAST Symposium on November 9, 2022



Visit to the University of Bordeaux in March 2023.
(Exchange meeting with Dr. Oda, Dr. Hano and Kyoto University students)

Universitat de València (UV), Spain

Prof. Barona-Vilar were invited to KU in Nov. and Dec. 2022. We had lectures for the COVID pandemic by him.



The 88th & 89th IROAST Seminar on November 29 and December 2.

Vytautas Magnus University (VMU), Lithuania

The total four collaborators associated with Prof. A. S. Maruska of VMU visited to KU in

Nov. 2022 and Mar. 2023. We discussed with research results for our Bilateral Joint Research Project of JSPS.

University of Dhaka (UD), Bangladesh

The collaborator, Assist. Prof. M. Shahrzaman of UD, was awarded for the Follow-up Research Fellowship of the Japan Student Services Organization (JASSO) with Prof. Takafuji as a host researcher, and conducted collaborative research at KU for about three months from September to November 2022.

Kyrgyz-Turkish Manas University (KTMU), Kyrgyz Republic

Assist. Prof. A. Mazhitova of KTMU was awarded for the Research Fellow of the Matsumae International Foundation (MIF) with Prof. Takafuji as a host researcher, and visited to KU for about six months from Jul. 2022 to Jan. 2023.

2-2. Maintaining international collaboration through remote-meetings and e-mail discussions
With

University of Geneva (UG), *Swiss Confederation (Switzerland)*,
Brookhaven National Laboratory (BNL), *United States of America*,
University of Connecticut (UC), *United States of America*,
Lanzhou Institute of Chemical Physics (LICP), *Chinese Academy of Sciences (CAS),
People's Republic of China*,
Beijing University of Chemical Technology (BUCT), *People's Republic of China*,
Noakhali Science and Technology University (NSTU), *People's Republic of Bangladesh*,
and
Baku State University (BSU), *Republic of Azerbaijan*

2-3. Publishing with international collaborators

Three and one joint papers have been published with researchers from UB and UD, respectively, in international journals. Also three joint papers have been published with Chinese researchers in international journals.

2-4. Grant projects regarding with international collaboration

- ✓ Fabrication of nano-to-submicron-sized exclusive pods and their spatial functionalization.
KAKEN, Fostering Joint International Research (B), JSPS. PI: Prof. M. Takafuji. Partner: R. Oda's groups of UB. FY 2019–2022.
- ✓ Circular polarization functions of chiral nano-structure integrated thermo-setting polymer films.
Bilateral Joint Research Project, JSPS. PI: Prof. M. Takafuji, Partner: Dr. Y. Ferrand and Dr. C. Olivier, who are LIA members of UB. FY 2022–2024
- ✓ Nano-architectural approach and empirical study realizing high-speed micro analysis for environmental samples using highly-ordered pi-electron materials.
Bilateral Joint Research Project, JSPS. PI: Prof. H. Ihara. Partner: Prof. A. Maruska's group of VMU. FY 2021–2022.
- ✓ Enantioselective nanobioimaging and biological application by fluorescent nanomaterials with controlled chiral space.
Bilateral Joint Research Project, JSPS. PI: Prof. H. Ihara. Partner: Prof. H. Qiu's group of LICP. FY 2022–2024.
- ✓ Development of monovalent ion selective ion exchange membranes based on polymer/MOF for salinity gradient energy production by reverse electrodialysis (RED).
Bilateral Joint Research Project, JSPS and TUBITAK (Turkey). PI: Prof. M. Takafuji. Partner: Dr. E. Guler's group of Atılım University (AU), Prof. N. Kabay's group of Ege

University (EU), Prof. A. Tuncel's group of Hacettepe University (HU) and Prof. M. Tominaga's group of Sage University (SU). FY 2022–2024.

- ✓ Investigation of protein fraction distribution during koumiss fermentation by ultra-selective HPLC.
Research Fellow from MIF. Dr. A. Mazhitova of **KTMU** with Prof. Takafuji as a host researcher. FY 2022 (extended from 2019).
- ✓ Development of cellulose nanocrystal/terpolymer hydrogel as an adsorbent for organic dye in wastewater.
Follow-up Research Fellowship from JASSO. Dr. M. Shahruzzaman of **UD** with Prof. Takafuji as a host researcher. FY 2022.

3. Research plan for the next year

We are planning to visit the international collaborators, attend international conferences and publish papers with the collaborators. We will also hold the first workshop for the Bilateral Joint Research Project of JSPS collaborated with Prof. H. Qiu's group of **LICP**, CAS, China, in Apr. 2023.

4. List of grants and patents

Accepted grants (On-going project)

- 4-1. FY 2021–2024: KAKEN, Grant-in-Aid for Scientific Research (B), JSPS, PI: **M. Takafuji**, Co-PI: **N. Hano**, 13,200,000 yen.
- 4-2. FY 2020–2022: KAKEN, Grant-in-Aid for Scientific Research (B), JSPS, PI: **H. Ihara**, Co-PI: **M. Takafuji**, S. Nagaoka, N. Okita, 13,700,000 yen.
- 4-3. FY 2022–2025: KAKEN, Grant-in-Aid for Scientific Research (B), JSPS, PI: T. Sagawa, Co-PI: **H. Ihara**, J. HWANG, K. Matsumoto, 15,400,000 yen.
- 4-4. FY 2018–2022: KAKEN, Fund for the Promotion of Joint International Research (Fostering Joint International Research (B)), JSPS, PI: **M. Takafuji**, Co-PI: **H. Ihara**, N. Ryu, **N. Hano**, 13,800,000 yen.
- 4-5. FY 2020–2022: KAKEN, Grant-in-Aid for Scientific Research (C), JSPS, PI: **Y. Kuwahara**, Co-PI: **H. Ihara**, N. Ryu, 3,300,000 yen.
- 4-6. FY 2022–2024: KAKEN, Grant-in-Aid for Scientific Research (C), JSPS, PI: T. Shirotsuki, Co-PI: **M. Takafuji**, N. Ryu, 3,200,000 yen.
- 4-7. FY 2020–2022: KAKEN, Grant-in-Aid for Scientific Research (C), JSPS, PI: N. Ryu, Co-PI: **M. Takafuji**, 3,400,000 yen.
- 4-8. FY 2020–2022: KAKEN, Grant-in-Aid for Scientific Research (C), JSPS, PI: K. Nishiyama, Co-PI: **M. Takafuji**, S. Yoshimoto, 3,400,000 yen.
- 4-9. FY 2020–2022: KAKEN, Grant-in-Aid for Challenging Research (Exploratory), JSPS, PI: **H. Ihara**, Co-PI: **Y. Kuwahara**, S. Nagaoka.
- 4-10. FY 2022–2024: KAKEN, Grant-in-Aid for Early-Career Scientists, JSPS, PI: **N. Hano**, 3,500,000 yen
- 4-11. FY 2022–2024: Bilateral Joint Research Projects with Turkey, JSPS, PI: **M. Takafuji**, 5,000,000 yen
- 4-12. FY 2022–2025: Bilateral Joint Research Projects with China, JSPS, PI: **H. Ihara**, 4,500,000 yen
- 4-13. FY 2022–2024: Bilateral Joint Research Projects with France (Open Partnership), JSPS,

PI: **M. Takafuji**, 4,000,000 yen

4-14. FY 2020–2021 (extended to 2022): Bilateral Joint Research Projects with Lithuania, JSPS, PI: **H. Ihara**, 5,000,000 yen.

4-15. FY 2022: MIF Fellow (from KTMU), Matsumae International Foundation, Host researcher: **M. Takafuji**, 1,000,000 yen

4-16. FY 2022: Follow-up Services for International Students who studied in Japan (from Univ. Teknologi Petronas, Malaysia), JASSO, Supervisor: **M. Takafuji**

Patent publication (Active)

4-17. Method for manufacturing column packing material for liquid chromatography, Inventor: R. Sun, S. Nozato, A. Nakasuga, **H. Ihara**, **M. Takafuji**, **Y. Kuwahara**, H. Noguchi, T. Liu, JP Patent: JP7061759B2

5. List of journal papers published between April 2022 and March 2023

5-1. Chiral H-aggregation-induced large Stokes shift with CPL generation assisted by α -helical poly(L-lysine) substructure
K. Yoshida, Y. Kuwahara, N. Hano, Y. Horie, M. Takafuji, N. Ryu, S. Nagaoka, R. Oda, H. Ihara
Chirality, web-published (doi: 10.1002/chir.23553), 2023.

5-2. Zwitterionic polymer-terminated porous silica stationary phases for highly selective separation in hydrophilic interaction chromatography
Y. Hu, J. Kadotani, Y. Kuwahara, H. Ihara, M. Takafuji
Journal of Chromatography A, 1693, 463885, 2023.

5-3. A π -extended phenanthrene-fused aza[7]helicene as a novel chiroptically-active architecture in organic and aqueous media
C. Olivier, N. Nagatomo, T. Mori, N. McClenaghan, G. Jonusauskas, B. Kauffmann, Y. Kuwahara, M. Takafuji, H. Ihara, Y. Ferrand
Organic Chemistry Frontiers, 10, 752-758, 2022.

5-4. Fabrication of naphthol-based phenolic polymer coated-silica for mixed-mode chromatography
Y. Hu, H. Ihara, M. Takafuji
Journal of Chromatography Open, 2, 100028, 2022.

5-5. Functionalized aluminum oxide by immobilization of totally organic aromatic polymer spherical nanoparticles
S. Nagaoka, K. Yoshida, Y. Hirota, Y. Komachi, M. Takafuji, H. Ihara
Colloids and Surfaces A: Physicochemical and Engineering Aspects, 640, 128438, 2022.

5-6. Preparation, chitosan/laterite/iron oxide-based biocomposite and its application as a potential adsorbent for the removal of methylene blue in aqueous solution
M. N. Sakib, N. Hano, M. Takafuji, S. Ahmed
Environmental Nanotechnology, Monitoring and Management, 17, 100658, 2022.

5-7. Co-assembling system that exhibits bright circularly polarized luminescence
N. Ryu, T. Harada, Y. Okazaki, K. Yoshida, T. Shirotsuki, R. Oda, Y. Kuwahara, M. Takafuji, H. Ihara, S. Nagaoka
Materials Advances, 3, 3123–3127, 2022.

5-8. Preparation of hybrid microspheres with homogeneously dispersed nanosilica using in-situ

sol-gel reaction inside a polystyrene matrix

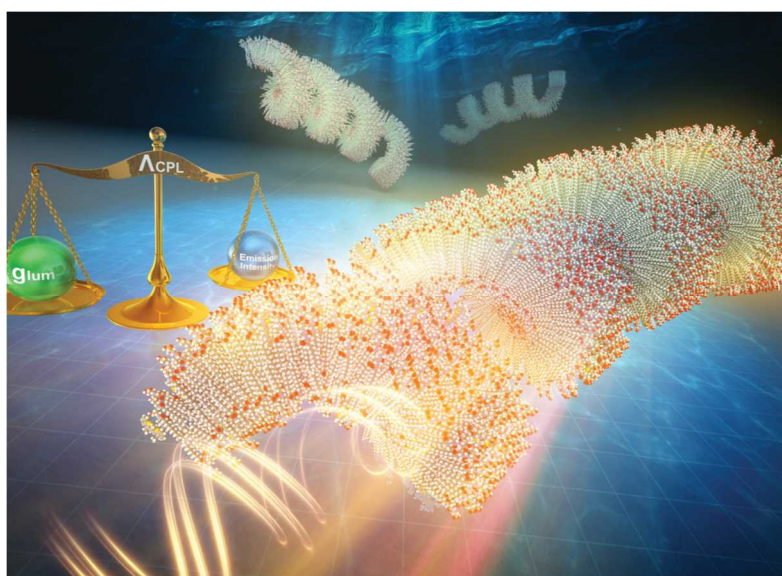
A. Toyofuji, N. Hano, Y. Yamaguchi, T. Wakiya, H. Ihara, M. Takafuji
Chemistry Letters, 51, 639-642, 2022.

5-9. Advanced CNC/PEG/PDMS semi-IPN hydrogel for drug delivery management in wound healing

S. Afrin, M. Shahruzzaman, P. Haque, M. S. Islam, S. Hossain, T. U. Rashid, T. Ahmed, M. Takafuji, M. M. Rahman
Gels, 8, 340-340, 2022.

5-10. Carbonized π -conjugated polymer-coated porous silica: preparation and evaluating its extraction ability for berberine


P. Jin, F. Zhu, M. Jiang, M. Takafuji, H. Ihara, L. Nie, H. Liu
Microchimica Acta, 189, 401, 2022.



Back Cover from *Materials Advances* (*Mater. Adv.*, Vol. 3, pp. 3123–3127, 2022), Royal Society of Chemistry.

<https://pubs.rsc.org/en/content/articlelanding/2022/ma/d2ma90038f>

FY2022 IROAST Research Cluster Activities Report

No.4-7	Nano-medicine and Drug Delivery System			
Cluster Coordinator				
Name	Hamid HOSANO	Title	Professor	
Affiliation E-mail	Institute of Industrial Nanomaterials (IINa) Email: hamid@kumamoto-u.ac.jp			
Research Field	Biotechnology & healthcare technology / Environment-friendly technology			
Cluster Members				
Name	Affiliation/Title			
Nushin HOSANO	Biomaterials and Bioelectrics Division, Institute of Industrial Nanomaterials Visiting Associate Professor			
Konstantinos KONTIS	School of Engineering, University of Glasgow, UK / Professor/ Dean for Global Engagement East-Asia&China / IROAST Visiting Professor			
Firus ZARE	Queensland University of Technology, Australia Professor/ Head of School Electrical Engineering and Robotics / IEEE Fellow / IROAST Visiting Professor			
Viren Ivor MENEZES	Department of Aerospace Engineering, Indian Institute of Technology Bombay, India Professor / IROAST Visiting Professor			
Hamid GHANDEHARI	Director of Utah Center for Nanomedicine/ Chair of Department of Pharmaceutics and Pharmaceutical Chemistry and Bioengineering, University of Utah, USA Professor / IROAST Visiting Professor			
Amir A. FARAJIAN	Department of Mechanical and Materials Engineering, Wright State University, USA Professor / IROAST Visiting Professor			
Pouyan BOUKANY	Department of Chemical Engineering, Faculty of Applied Sciences, Delft University of Technology, Netherlands Associate Professor / IROAST Visiting Professor			
Stelios RIGOPOULOS	Department of Mechanical Engineering, Imperial College London, UK Reader / IROAST Visiting Professor			

Details of activities

We have been studying the use of physical delivery of drug or reprogramming factors into the cells and tissue, as a safe and reliable method. Our needle-free pain-free disposable vaccine/drug delivery microjet injection has been steadily progressing. We have also been exploring integrated diagnostic and therapeutic (theranostics) modalities/nanoparticles/agents, as a unique approach in nanomedicine. The research has potential to be used in a wide range of medical applications.

Our physical delivery approaches are based on applying electrical/mechanical stresses to the cells.

In this respect, attention has been made to understand biophysical reactions to reversibly manipulate the cells by the external stress. We have been investigating promising physical delivery methods including: needle-free painless microinjection, electroporation with nanosecond pulsed electric fields, micro/nano-particle carrier laser-biostic delivery, sonoporation with microfluidics, and shock waves; which are shown to be appropriate for clinical applications. Particularly we had progress in pain-free non-invasive drug delivery and diagnostic.

During the first six months of the year 2022, due to travel and other restrictions brought by the COVID-19 pandemic, we could not travel or have presence of our Visiting Professors in Kumamoto University. Meanwhile, with easing restrictions and with support of IROAST, Hosano could visit Prof. Stelios Rigopoulos at Imperial College London during August 2022 and Prof. Kontis at the University of Glasgow during February 2023, for joint research and publication. The Cluster welcomed new members, Prof. Stelios Rigopoulos, from Department of Mechanical Engineering, Imperial College London, UK; and Prof. Pouyan Boukany, from Delft University of Technology, Netherlands. Their presence will promote our projects and will help the Cluster to further achieve its goals.

We will continue our fruitful discussions and collaboration with the cluster members for a joint projects and budget applications.

Our new generation of therapeutic nanoparticles work with Prof. Moosavi-Nejad and Prof. Rigopoulos will continue for the next fiscal year. We also started closer collaboration with them for protein nanoparticles.

Awards:

The Carlsberg Foundation “Senior Researcher Award” August 2022 (World Congress on Electroporation), Hamid Hosano

Grants:

Grants-in-Aid for Scientific Research, Kakenhi (B), 2021-2025

Joint International publications resulted from IROAST International Internships:

M. Pakdel, Z. Moosavi-Nejad, R. K. Kermanshahi, H. Hosano,
Self-assembled uniform keratin nanoparticles as building blocks for nanofibrils and
nanolayers derived from industrial feather waste,
Journal of Cleaner Production, 335 130331-130331, 2022
DOI: [10.1016/j.jclepro.2021.130331](https://doi.org/10.1016/j.jclepro.2021.130331)

Farzan Zare, Negareh Ghasemi, Nidhi Bansal, Hamid Hosano
Advances in pulsed electric stimuli as a physical method for treating liquid foods
Physics of Life Reviews 44 207-266, Feb 2023
DOI: [10.1016/j.plrev.2023.01.007](https://doi.org/10.1016/j.plrev.2023.01.007)


Joint International publication:

Nushin Hosano, Zahra Moosavi-Nejad, Makoto Satoh, Hamid Hosano,
Shock Waves Enhance Expression of Glycosphingolipid Tumor Antigen on Renal Cell
Carcinoma: Dynamics of Physically Unmasking Hidden Intracellular Markers Independent
of Gene-Signaling Pathways,
Biomedicines, 10(3) 545-545, 2022
DOI: [10.3390/biomedicines10030545](https://doi.org/10.3390/biomedicines10030545)

Other publications:

Md. Mijanur Rahman, Nushin Hosano, Hamid Hosano,
Recovering Microalgal Bioresources: A Review of Cell Disruption Methods and Extraction
Technologies, *Molecules*, 27(9) 2786-2817, 2022
DOI: 10.3390/molecules27092786

FY2022 IROAST Research Cluster Activities Report

No.4-8	Nano-medicine and Theranostics			
Cluster Coordinator				
Name	Takuro NIIDOME	Title	Professor	
Affiliation E-mail	Faculty of Advanced Science and Technology (FAST) Email: niidome@gpo.kumamoto-u.ac.jp			
Research Field	Biotechnology & healthcare technology			
Cluster Members				
Name	Affiliation/Title			
Ick Chan KWON	Biomedical Research Institute, Korea Institute of Science and Technology (KIST), Korea Principal Research Scientist			
Ruda LEE	Institute of Industrial Nanomaterials Associate Professor			
Keiichi MOTOYAMA	Faculty of Life Sciences Professor			
Taishi HIGASHI	Priority Organization for Innovation and Excellence Associate Professor			

1) Overview of achievements

Theranostics is a rapidly developing field that combines the unique opportunities offered by nanotechnology with personalized medicine to provide significantly improved treatment efficacy with reduced off-target effects through specific therapy delivery to targeted tissues. These approaches combine imaging that uses one of the non-invasive imaging modalities, with specific delivery of therapeutic components, which can be based on different biophysical and biological principles. Theranostics can be synthesized to have optimal delivery properties, low renal clearance, reduced immunogenicity, and antigenicity (for example, by PEGylating the surface of theranostic nanoparticles), and high capacity for therapeutic agents is required given the limited concentrations of specific molecular markers expressed on cancer cells.

This research unit focuses on developing a diagnosis and drug delivery system for biomedical applications. The research unit's interdisciplinary research collaboration with engineers, pharmacists, and clinicians can improve a deeper knowledge and understanding of the real interactions involved in diseased tissues is fundamental for developing novel therapeutic approaches. In this fiscal year, we suggest a new paradigm for cardiac reprogramming, multi-targeting gene delivery systems, and many other theranostics nanomedicine platforms.

2) Presentations & Publications published between April 2022 and March 2023

Takuro NIIDOME

[Presentations]

1. **Takuro Niidome**, Anna Kawano, Sayaka Sawada, Tatsuya Baba, Makoto Sasaki, Wei Xu, Graphene Quantum Dots as a Biomaterial: Synthesis and Use of Anti-bacterial and Anti-viral Agents, 44th Annual Meeting of Japanese Society, 2022/11/21, Tokyo, Japan
2. **Takuro Niidome**, Ryoko Nawata, Emi Takeda, Ryosuke Suzuki, Wei Xu, Preparation of Silver Nanoplates Encapsulated in PLGA Nanoparticles and Control of their Antibacterial Activity by Laser Light, 38th Annual Meeting of the Japanese Society for Drug Delivery System, Online

[Publications]

1. Waliul Islam, Hiroyasu Tsutsuki, Katsuhiko Ono, Ayaka Harada, Kozo Shinozaki, **Takuro Niidome**, Jun Fang, Tomohiro Sawa, Structural determination of the nanocomplex of borate with styrene-maleic acid copolymer-conjugated glucosamine used as a multifunctional anticancer drug, *ACS Appl. Bio Mater.*, 12, 5953–5964 (2022)
2. Waliul Islam, **Takuro Niidome**, Tomohiro Sawa, The enhanced permeability and retention effect as a ubiquitous and epoch-making phenomenon in the selective targeting of drugs to solid tumors, *J. Pers. Med.*, 12, 1964 (2022)
3. Yuko T Sato, Daisuke Asai, Keiko Terada, Jeong-Hun Kang, Takeshi Mori, **Takuro Niidome**, Hideki Nakashima, Yoshiki Katayama, A model of transcriptional activation of DNA by loosening of chromatin structure, *Chem. Lett.*, 51, 1109–1112 (2022)
4. Ayaka Harada, Hiroyasu Tsutsuki, Tianli Zhang, Kinnosuke Yahiro, Tomohiro Sawa, **Takuro Niidome**, Controlled delivery of an anti-inflammatory toxin to macro-phages by mutagenesis and nanoparticle modification, *Nanomaterials*, 12, 2161 (2022)
5. Makoto Sasaki, Wei Xu, Yuki Koga, Yuki Okazawa, Akira Wada, Ichiro Shimizu, **Takuro Niidome**, Effect of parylene C on the corrosion resistance of bioresorbable cardiovascular stents made of magnesium alloy 'Original ZM10', *Materials*, 15, 3132 (2022)
6. Mai Shinohara, Wei Xu, Sun-nam Kim, Tuyoshi Fukaminato, **Takuro Niidome**, Seiji Kurihara, Photo-control of cellular uptake by the selective adsorption of spiropyran derivatives on albumin, *Chem. Lett.*, 51, 594–597 (2022)
7. Wei Xu, Makoto Sasaki, **Takuro Niidome**, Sirolimus release from biodegradable polymers for coronary stent, *Pharmaceutics*, 14, 492 (2022)
8. Emi Takeda, Wei Xu, Mitsuhiro Terakawa, **Takuro Niidome**, Tailored structure and antibacterial properties of silica-coated silver nanoplates by pulsed laser irradiation, *ACS Omega*, 7, 7251–7256 (2022)
9. Mai Shinohara, Yuya Ashikaga, Wei Xu, Sunnam Kim, Tuyoshi Fukaminato, **Takuro Niidome**, Seiji Kurihara, Photochemical OFF/ON cytotoxicity switching by using a photochromic surfactant with visible light irradiation, *ACS Omega*, 7, 6093–6098 (2022)

[Presentations]

1. **Ruda Lee**, Emerging Role of Nanotechnology for Water Sustainability. Korea International Water Week (KIWW) 2022. 2022/11/24, Daegu, Korea.



(Dr. Ruda LEE in the center)



(Group Photo at the venue)

2. **Ruda Lee**, Nanoplatform for constructing new approaches to cancer treatment. Kangwon National University, 2022/03/30, Web.

[Publications]

1. Strategic Review of Germany's LULUCF Policy Development Process: Implications for Korea. Woojin Lee Leehyung Kim, **Ruda Lee***. *Journal of Wetlands Research*, 2022, 24, 102-114.

Ick Chan KWON

[Presentations]

N/A

[Publications]

1. Improved survival rate and minimal side effects of doxorubicin for lung metastasis using engineered discoidal polymeric particles. Sanghyo Park, Hyungkyu Park, Chaewon Park, Wan Su Yun, Soonjae Hwang, Hong Yeol Yoon, **Ick Chan Kwon**, Kwangmeyung Kim, Jaehong Key. *Biomater, Sci.*, 2022, 10, 4335-4344.
2. Ultraefficient extracellular vesicle-guided direct reprogramming of fibroblasts into functional cardiomyocytes. Hyosuk Kim, Byeong-Wook Song, Soon-Jung Park, Seong Woo Choi, Hanbyeol Moon, Ki-Chul Hwang, Sun-Woong Kang, Sung-Hwan Moon, Yoosoo Yang, **Ick Chan Kwon***, Sun Hwa Kim. *Science Advances*, 2022,8, eabj6621.
3. PDL1-binding peptide/anti-miRNA21 conjugate as a therapeutic modality for PD-L1high tumors and TAMs. Eun Hye Kim, Jongwon Lee, Gijung Kwak, Hochung Jang, Hyosuk Kim, Haeun Cho, Yeongji Jang, Jiwoong Choi, Sung-Gil Chi, Kwangmeyung Kim, **Ick Chan Kwon**, Yoosoo Yang, Sun Hwa Kim. *J. Controlled Release*, 2022, 345, 62-74.
4. Exosome-guided direct reprogramming of tumor-associated macrophages from protumorigenic to antitumorigenic to fight cancer. Hyosuk Kim, Hyun-Ju Park, Hyo Won Chang, Ji Hyun Back, Su Jin Lee, Yae Eun Park, Eun Hye Kim, Yeonsun Hong, Gijung Kwak, **Ick Chan Kwon**, Ji Eun Lee, Yoon Se Lee, Sang Yoon Kim, Yoosoo Yang, Sun Hwa Kim. *Bioactive Materials*, 2023, 25, 527-540.
5. Molecularly engineered siRNA conjugates for tumor-targeted RNAi therapy. Jong Won Lee, Jiwon Choi, Yeonho Choi, Kwangmeyung Kim, Yoosoo Yang, Sun Hwa Kim, Hong Yeol Yoon, **Ick Chan Kwon***. *J. Controlled Release*, 2022, 351, 713-726.
6. Intracellular Glucose-Depriving Polymer Micelles for Anti-Glycolytic Cancer Treatment. Jangwook Lee, Kwangmeyung Kim, **Ick Chan Kwon**, Kuen Yong Lee. *Advanced materials*, 2022, 35, 2207342.

Keiichi MOTOYAMA & Taishi HIGASHI

[Presentations]

1. Masamichi Inoue, Takashi Saito, Takaomi C. Saido, Risako Onodera, **Taishi Higashi**, **Keiichi Motoyama**, Hirofumi Jono, Design and Evaluation of shRNA Polyplex with Cyclodextrin-modified Dendrimer for Treatment of Systemic and Localized Amyloidosis, The 18th International Symposium on Amyloidosis (online), Heidelberg, Germany, September 4-8 (2022).
2. Masamichi Inoue, Takashi Saito, Takaomi C. Saido, Risako Onodera, **Taishi Higashi**, **Keiichi Motoyama**, Hirofumi Jono Feasibility Study of Cationic Dendrimer-based Polyplex as a Multi-functional Drug for Alzheimer's Disease, The 3rd International Conference on Advanced Materials and Nanotechnology, Singapore, August 18-19 (2022).
3. Yoshitaka Ohno, Maiko Toshino, Yukio Fujiwara, Yoshihiro Komohara, Risako Onodera, **Taishi Higashi**, **Keiichi Motoyama**, Dual-targeting for Colon Cancer Cells and Tumor-Associated Macrophages by Mannose- modified Methyl- β -Cyclodextrins as Antitumor Therapeutic Agents, The 3rd International Conference on Advanced Materials and Nanotechnology, Singapore, August 18-19 (2022).



(Awarded at the conference)



(Meal time at Singapore)

[Publications]

1. Y. Ohno, M. Toshino, A. F. A. Mohammed, Y. Fujiwara, Y. Komohara, R. Onodera, **T. Higashi**, **K. Motoyama**. Mannose-methyl- α -cyclodextrin suppresses tumor growth of colon cancer by targeting tumor-associated macrophages. *Carbohydr. Polym.*, 305, 120551 (2023).
2. A. Sakai, Y. Yamashita, S. Misumi, N. Kishimoto, R. Onodera, **T. Higashi**, H. Arima, **K. Motoyama**, Nanoparticle composites of folic acid-modified methyl- α -cyclodextrin and adamantane/human serum albumin for enhanced antitumor activity. *FEBS Open Bio*, 13, 233-245 (2023).

3. A. F. A. Mohammed, M. H. Othman, T. Taharabaru, K. M. Elamin, K. Ito, M. Inoue, M. El-Badry, K. I. Saleh, R. Onodera, **K. Motoyama**, **T. Higashi**, Stabilization and movable ligand-modification by folate-appended polyrotaxanes for systemic delivery of siRNA polyplex. *ACS Macro. Lett.*, 11, 1225-1229 (2022).
4. T. Hayashi, F. Nakagawa, Y. Ohno, Y. Suzuki, H. Ishiki, R. Onodera, **T. Higashi**, Y. Shimamura, H. Itou, Y. Iwase, H. Arima, **K. Motoyama**, Antigen stabilizing hydrogels based on cyclodextrins and polyethylene glycol act as type-2 adjuvants with suppressed local irritation. *Eur. J. Pharm. Biopharm.*, 181, 113-121 (2022).
5. Y. Yamada, T. Miwa, M. Nakashima, A. Shirakawa, N. Namba, Y. Kondo, T. Takeo, N. Nakagata, **K. Motoyama**, **T. Higashi**, H. Arima, Y. Kurauchi, T. Seki, H. Katsuki, Y. Okada, A. Ichikawa, K. Higaki, K. Hayashi, K. Minami, N. Yoshikawa, R. Ikeda, Y. Ishikawa, T. Kajii, K. Tachii, H. Takeda, Y. Orita, M. Matsuo, T. Irie, Y. Ishitsuka, Fine-tuned cholesterol solubilizer, mono-6-*O*- α -D-maltosyl- α -cyclodextrin, ameliorates experimental Niemann-Pick disease type C without hearing loss. *Biomed. Pharmacother.*, 155, 113698 (2022).
6. M. Inoue, **T. Higashi**, Y. Hayash, R. Onodera, K. Fujisawa, T. Taharabaru, R. Yokoyama, K. Ouchi, Y. Misumi, M. Ueda, Y. Inoue, M. Mizuguchi, T. Saito, T. Saido, Y. Ando, H. Arima, **K. Motoyama**, H. Jono, Multifunctional therapeutic cyclodextrin-appended dendrimer complex for treatment of systemic and localized amyloidosis. *ACS Appl. Mater. Interfaces*, 14, 40599-40611 (2022).
7. M. Inoue, K. Muta, A. F. A. Mohammed, R. Onodera, **T. Higashi**, K. Ouchi, M. Ueda, Y. Ando, H. Arima, H. Jono, **K. Motoyama**, Feasibility study of Dendrimer-based TTR-CRISPR pDNA polyplex for ocular amyloidosis in vitro. *Biol. Pharm. Bull.*, 45, 1660-1668 (2022).
8. F. Nakagawa, Y. Shimamura, Y. Suzuki, T. Taharabaru, H. Itou, Y. Iwase, R. Onodera, **T. Higashi**, **K. Motoyama**, Application of cyclodextrin/polyethylene glycol in blood-storage tools for liquid biopsy. *Mater. Lett.*, 324, 132660 (2022).
9. Y. Nakatani, Z. Ye, Y. Ishizue, **T. Higashi**, T. Imai, I. Fujii, M. Michigami, A 'human and mouse cross-reactive' albumin-binding helix-loop-helix peptide tag for prolonged bioactivity of therapeutic proteins. *Mol. Pharm.*, 19, 2279-2286 (2022).
10. T. Nishida, R. Yokoyama, Y. Kubohira, Y. Maeda, T. Takeo, N. Nakagata, H. Takagi, K. Ishikura, K. Yanagihara, S. Misumi, N. Kishimoto, Y. Ishitsuka, Y. Kondo, T. Irie, M. Soga, T. Era, R. Onodera, **T. Higashi**, **K. Motoyama**, Lactose-appended hydroxypropyl- α -cyclodextrin ameliorates hepatosplenomegaly in Niemann-Pick Type C Disease by lowering cholesterol. *ACS Appl. Bio Mater.*, 5, 2377-2388 (2022).
11. **T. Higashi**, **K. Motoyama**, J. Li, Cyclodextrin-based catenanes and polycatenanes. *J. Incl. Phenom. Macrocycl. Chem.*, 102, 569-575 (2022).
12. T. Taharabaru, T. Kihara, R. Onodera, T. Kogo, K. Higashi, K. Moribe, T. Nakamura, **K. Motoyama**, **T. Higashi**, Polyrotaxane-based multi-step transformable materials for the delivery of Cas9 ribonucleoprotein. *Appl. Mater. Today*, 27, 101488 (2022).
13. Y. Sadahiro, Y. Hitora, I. Kimura, N. Hitora-Imamura, R. Onodera, **K. Motoyama**, S. Tsukamoto, Colletofragarone A2 Inhibits Cancer Cell Growth In Vivo Leads to the Degradation and Aggregation of Mutant p53. *Chem. Res. Toxicol.*, 9, 1598-1603 (2022).

3) Application & acquisition status of KAKENHI and other external grants

Takuro Niidome

1. FY2021 JSPS, Grant-in-Aid for Challenging Research (Exploratory)
2. FY2022 Grant-in-Aid for Scientific Research (B)
3. FY2018 JST, CREST
4. FY2018 AMED

Ruda LEE

1. FY2022 JSPS, Grant-in-Aid for Scientific Research (C)
2. FY2021 AMED, Infectious Diseases and Immunology Research: U.S.-Japan Cooperative Medical Sciences Program Collaborative Awards
3. Brain Pool Korea 2022

Ick Chan KWON

: N/A

Keiichi MOTOYAMA & Taishi HIGASHI

1. FY2021 JSPS Grant-in-Aid for Scientific Research (C) (K. Motoyama)
2. FY2022 Grant-in-Aid for Scientific Research (B) (T. Higashi)
3. A-step Ikuseigata (T. Higashi)
4. The Leading Initiative for Excellent Young Researchers (T. Higashi)

4) Application & acquisition status of industrial property rights

Takuro Niidome

: N/A

Ruda Lee

: N/A


Ick Chan KWON

1. Sun Hwa Kim, **Ick Chan Kwon**, In-San Kim, KIM Kwangmeyung, YANG Yoosoo, Young-ji Ko. Immunoregulatory protein-siRNA complex having anticancer activity. US Patent application 2022-16573351.

Keiichi MOTOYAMA & Taishi HIGASHI

1. **Taishi Higashi, Keiichi Motoyama**, Risako Onodera, Yoshitaka Matsumoto, Boronic acid-appended Polyrotaxane, Patent application 2022-46218.

FY2022 IROAST Research Cluster Activities Report

No.4-9	Multiscale Modeling of Soil and Rock Materials Using X-ray CT			
Cluster Coordinator				
Name	Jun OTANI	Title	Professor	
Affiliation E-mail	Faculty of Advanced Science and Technology (FAST) E-mail : junotani@kumamoto-u.ac.jp			
Research Field	Environment-friendly technology / Strengthening resilience			
Cluster Members				
Name	Affiliation/Title			
Gioacchino VIGGIANI	Professor/ IROAST Visiting Professor, University of Grenoble Alpes France			
José E. ANDRADE	George W. Housner Professor of Civil and Mechanical Engineering, Cecil and Sally Drinkward Leadership Chair, Executive Officer for Mechanical and Civil Engineering, Engineering and Applied Science Division, California Institute of Technology /IROAST Visiting Professor USA			

[Details of activities]


1. Research outline and its perspective

The topic of this research unit is the application of x-ray imaging to engineering, especially for geomaterials (soils, rock, and concrete). X-ray imaging plays a key role for the experimental multi-scale analysis of geomechanics, in that it helps linking the mechanisms occurring at the micro scale to the mechanical behavior observed at the macro scale. The research unit includes three top-ranked groups in geomechanics.

2. Research progress and results in the fiscal year (attach 1-2 related photos)

We sent a student to Prof. Viggiani's research lab in University of Grenoble Alpes for a year last year, and that student completed the master's degree in March, 2023 and start studying again there as a regular PhD student in this fall. The student's research results are currently being prepared for submission to a European journal. The paper will be submitted by the time the student goes abroad.

FY2022 IROAST Research Cluster Activities Report

No.4-10	Micro CT-based quantification of fibrosis and vascularization in pancreatic tumor			
Cluster Coordinator				
Name	Toshifumi MUKUNOKI	Title	Professor	
Affiliation E-mail	Faculty of Advanced Science and Technology (FAST) E-mail : mukunoki@kumamoto-u.ac.jp			
Research Field	Biotechnology & healthcare technology / Environmental bioscience / Data science and AI			
Cluster Members				
Name	Affiliation/Title			
Jun OTANI	Faculty of Advanced Science and Technology (FAST), Kumamoto University Professor			
Takatsugu ISHIMOTO	IRCMS, Kumamoto University Professor			
Patrice DELMAS	The University of Auckland, New Zealand Associate Professor			

[Details of activities]

1. Research outline and its perspective

The fibrotic tumor microenvironment is widely considered to be hypovascular; however, we found that the angiogenesis level is maintained in 15-pgdh^{+/-} mice, and these changes were also observed in a genetically engineered PDAC mouse model. Further confirmation revealed that fibroblast growth factor 1 (FGF1) is secreted by pancreatic cancer cells after PGE2 stimulation, consequently promoting CAF proliferation and vascular endothelial growth factor A (VEGFA) expression in the tumor microenvironment. Finally, in 15-pgdh^{+/-}Acta2-TK mice, depletion of fibroblasts inhibited angiogenesis and cancer cell viability in orthotopically transplanted tumors. These findings highlighted the role of 15-pgdh downregulation in enhancing PGE2 accumulation in the pancreatic tumor microenvironment and in subsequently maintaining the angiogenesis level in fibrotic tumors along with CAF expansion.

2. Research progress and results in the fiscal year (attach 1-2 related photos)

Inflammation and cancer are closely related and favor each other mutually. We were aiming to find the connection between pancreatic cancer and arachidonic cascade, in which we knocked out the key enzyme 15pgdh in mice and established an inflammatory syngeneic mouse model. Arachidonate cascade is a major inflammatory pathway that produces prostaglandin E2 (PGE2). We have reported that accumulation of PGE2 in 15pgdh KO mouse promoted cancer stem cell fraction and tumor formation (Arima et al. *Oncogene*). In

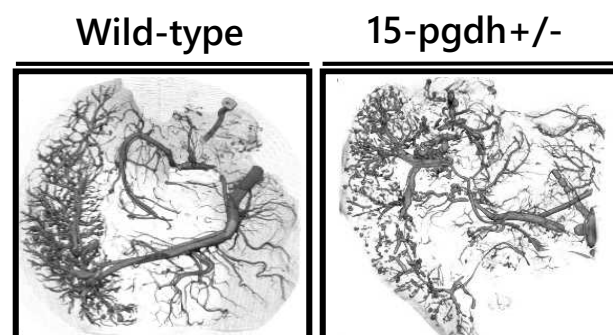


Figure 1 Nano-CT image of tumor

KO mouse promoted cancer stem cell fraction and tumor formation (Arima et al. *Oncogene*). In

current project we found out that angiogenesis level is promoted by depletion of 15pgdh in tumor microenvironment, and have already confirmed enhancement of vascular structure in 15pgdh+/- mouse comparing to wildtype mouse by NanoCT (Figure 1). Based on the finding, we proved that inflammation related PGE2 signaling enhances tumor angiogenesis in pancreatic tumor formation.

3. Research plan for the next year

We published one journal paper and so we will close this cluster in 2022.


4. List of awards, grants, and patents, if any.

None

5. List of journal papers published between April 2022 and March 2023

Bu L, Yonemura A, Yasuda-Yoshihara N, Uchihara T, Ismagulov G, Takasugi S, Yasuda T, Okamoto Y, Kitamura F, Akiyama T, Arima K, Itoyama R, Zhang J, Fu L, Hu X, Wei, F, Arima Y, Moroishi T, Nishiyama K, Sheng G, Mukunoki T, Otani J, Baba H, Ishimoto T*. Tumor microenvironmental 15-PGDH depletion promotes fibrotic tumor formation and angiogenesis in pancreatic cancer *Cancer Sci.* 2022 Oct;113(10):3579-3592.

FY2022 IROAST Research Cluster Activities Report

No.4-11	Quantification of Three Dimensional Vascular Network			
Cluster Coordinator				
Name	Toshifumi MUKUNOKI	Title	Professor	
Affiliation E-mail	Faculty of Advanced Science and Technology (FAST) E-mail : mukunoki@kumamoto-u.ac.jp			
Research Field	Biotechnology & healthcare technology / Environmental bioscience			
Cluster Members				
Name	Affiliation/Title			
Yuichiro ARIMA	IRCMS, Developmental Cardiology, Associate Professor (PI)			
Jun OTANI	Faculty of Advanced Science and Technology (FAST), Kumamoto University Professor			
Patrice DELMAS	The University of Auckland, New Zealand Associate Professor			

[Details of activities]

1. Research outline and its perspective (approximately 50-80 words and attach 1-2 relevant photographs)

This study aims to visualize the fine structure of mouse tissues using nano-X-ray CT and quantitatively evaluate the obtained three-dimensional image information. The research focuses on the potential applications of nano-X-ray CT (Figure1) in the biomedical field, specifically in understanding the microstructure of tissues. The use of this technology has the potential to revolutionize the study of the biological structure of tissues and could lead to significant advances in the medical field.



Figure1. Nano X-ray CT

2. Research progress and results in the fiscal year

In the fiscal year 2022, we used the nano X-ray CT (SkyScan 2214, Bruker Co. Ltd) installed at the Kumamoto University X-Earth Center to attempt to establish optimal imaging conditions. We used mouse embryos (Figure2), neonatal mouse hearts, and adult mouse hearts as samples and adjusted the voltage and current settings to produce images of the fine structure. We successfully visualized blood vessels with diameters as small as 10 microns by injecting contrast agents into the vessels. We also achieved high-contrast imaging of the myocardium by staining it with Lugol's solution.

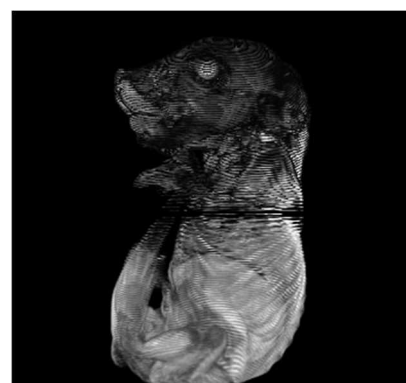


Figure2. Nano X-ray CT image of mouse embryo

3. Research plan for the next year

Although we have made progress in visualizing blood vessels using Nano-CT, the viscosity of the contrast agent has hindered adequate perfusion in small blood vessels. Therefore, we aim to adjust the formulation of the contrast agent or introduce new agents to visualize the entire microcirculation. Furthermore, we plan to develop a quantitative evaluation method using the obtained three-dimensional images. Our ultimate goal is to contribute to the advancement of the biomedical field by providing a comprehensive understanding of the microstructure of tissues through nano-X-ray CT.

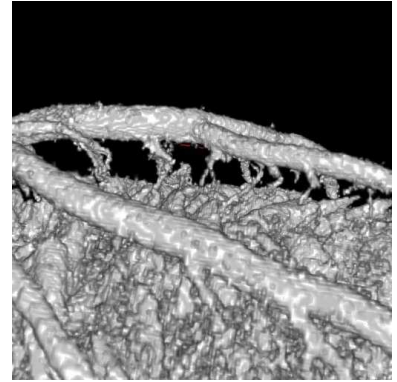


Figure3. Maximum resolution of blood vessels


4. List of awards, grants, and patents, if any.

Yuichiro Arima has been selected as a JST-PRESTO (さきがけ) Researcher for the fiscal year 2022.

5. List of journal papers (with IROAST as your affiliation) published between April 2022 and March 2023

Under working

FY2022 IROAST Research Cluster Activities Report

No.4-12	Advanced Structural Materials			
Cluster Coordinator				
Name	Yoji MINE	Title	Professor	
Affiliation E-mail	Faculty of Advanced Science and Technology (FAST) E-mail : mine@msre.kumamoto-u.ac.jp			
Research Field	Advanced materials			
Cluster Members				
Name	Affiliation/Title			
Yufeng ZHENG	School of Materials Science and Engineering, Peking University, China / Professor & IROAST Distinguished Professor			
Paul BOWEN	School of Metallurgy and Materials, University of Birmingham, UK / Feeney Professor of Metallurgy & IROAST Visiting Professor			
Yu-Lung CHIU	School of Metallurgy and Materials, University of Birmingham, UK / Reader in Physical Metallurgy			
Hiroto KITAGUCHI	School of Metallurgy and Materials, University of Birmingham, UK / Senior Research Fellow			
Martin DIENWIEBEL	Applied Nanotribology, Karlsruhe Institute for Technology (KIT), Germany / Heisenberg-Professor & IROAST Visiting Professor			
Shirley SHEN	CSIRO, Australia / Principal Research Scientist & IROAST Visiting Professor			
Kazuki TAKASHIMA	IROAST, Kumamoto University, Japan / Distinguished Professor			
Kwangsik KWAK	Faculty of Advanced Science and Technology, Kumamoto University, Japan / Assistant Professor			

[Details of activities]

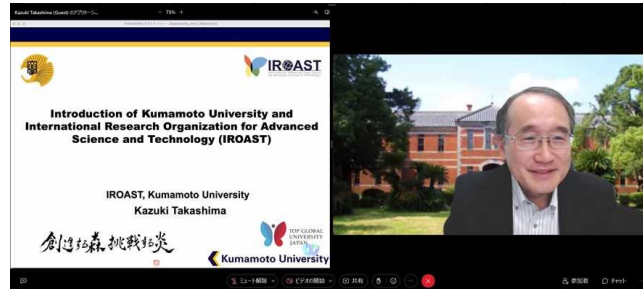
1. Research outline and its perspective

The mechanical properties of materials are dominated by their microstructures such as grain size, precipitates, phase boundary, grain boundary, etc. In our research group, we aim to clarify the mechanical properties at microscopic level, including tensile properties, fracture and fatigue properties, using the micromechanical testing technology that we have developed. Furthermore, in conjunction with crystal plasticity finite element simulation, we aim to predict the mechanical properties of bulk materials based on those at microscopic scale. The results obtained in this research will contribute for developing toughening design of advanced materials.

2. Research progress and results in the fiscal year

Unfortunately, due to the pandemic of COVIC-19, mutual exchanges were not possible in FY2022, and outcomes were limited. In spite of this situation, some new and valuable results were obtained. The international workshop between **CSIRO** and **KU** was held online in July to exchange information and ideas on the fabrication and mechanical characterization of advanced

materials. We have also collaborated with Professor **Bowen** and researchers (Dr. **Chiu** and Dr. **Kitaguchi**) at the **University of Birmingham (UoB)** to elucidate the mechanisms of plastic deformation and fatigue crack propagation in martensitic steel, titanium alloy and nickel superalloy using the micro-fatigue testing technique developed by KU. We have performed metallographic examination on the deformed microstructure of titanium alloy after fatigue in KU and have been preparing to write an international joint paper. Further, we started a collaborative study with Professor **Dienwiebel** at **KIT** to understand the effects of hydrogen on the micro-tribology and fatigue in bearing steels.



[The international workshop between CSIRO and KU (online) in July, 2022]

3. Research plan for the next year

We are planning to submit an international joint paper entitled “Effects of crystallographic orientation and lamellar configuration on the fatigue crack propagation in a single-colony structure of Ti-6Al-4V alloy” by “S. Ueki, Y. Mine, X. Lu, Y.L. Chiu, P. Bowen (UoB) and K. Takashima”. Professor **Mine** will participate in the international conference THERMEC 2023 in July to deliver a keynote lecture. Dr. **Kwak** will visit **KIT** from August to September to accelerate the collaborative study on the tribology/fatigue of bearing steel in hydrogen environment. Professor **Dienwiebel** will visit KU in September to write an international joint paper on the hydrogen embrittlement study of bearing steel.

4. List of awards, grants, and patents.


- (1) Elucidation of plastic deformation mechanism of additively manufactured Ti-6Al-4V alloys using trans-length scale mechanical characterization, KAKENHI Grant-in-Aid for Early-Career Scientists 2021-2024 (Continuing).
- (2) Development of local strengthening of micro-mechanical components using martensitic transformation induced by focused ion beam irradiation, KAKENHI Grant-in-Aid for Challenging Exploratory Research 2021-2022 (Continuing).
- (3) Elucidation of fatigue crack growth mechanism of martensite steels using micro-mechanical testing technique and application to fatigue strengthening design, KAKENHI Grant-in-Aid for Scientific Research (A) 2020-2024 (Continuing).

5. List of journal papers (with IROAST as your affiliation) published between April 2022 and March 2023

- (1) **K. Kwak, Y. Mine, S. Morito, T. Ohmura, K. Takashima:**
Correlation between strength and hardness for substructures of lath martensite in low- and medium-carbon steels
Materials Science and Engineering A, 856 (2022) 144007.
- (2) Y. Tampa, K. Takagi, S. Ueki, M. Ohta, **Y. Mine, K. Takashima:**
Comparative study of shear fracture between Fe-based amorphous and ultrafine-grained alloys using micro-tensile testing
ISIJ International, 62 (2022) 1741-1749.
- (3) **K. Kwak, Y. Okamura, Y. Mine, K. Takashima, S. Koseki, S. Ando, K. Kuwabara:**
Micro-mechanical characterisation of slip behaviour and precipitation strengthening in

CoCrFeNiTiMo alloy additively manufactured by laser powder bed fusion
Materials Science and Engineering A, 840 (2022) 142970.

FY2022 IROAST Research Cluster Activities Report

No.4-13	Microstructure Analysis and Grain Boundary Engineering			
Cluster Coordinator				
Name	Sadahiro TSUREKAWA	Title	Professor	
Affiliation E-mail	Faculty of Advanced Science and Technology (FAST) E-mail : turekawa@kumamoto-u.ac.jp			
Research Field	Advanced materials			
Cluster Members				
Name	Affiliation/Title			
Dmitri Aleks MOLODOV	Institute of Physical Metallurgy and Metal Physics, RWTH Aachen University, Germany Professor, IROAST Distinguished Professor			
Pavel LEJČEK	Institute of Physics, Academy of Sciences of the Czech Republic / University of Chemistry and Technology, Prague, Czech Republic Professor, IROAST Visiting Professor			
Mitsuhiro MATSUDA	Faculty of Advanced Science and Technology (FAST) Associate Professor			
Thomas WAITZ	Faculty of Physics, University of Vienna, Austria Associate Professor, IROAST Visiting Professor			
Christian RENTENBERGER	Faculty of Physics, University of Vienna, Austria Associate Professor, IROAST Visiting Professor			
Yoshitaka MATSUKAWA	Faculty of Advanced Science and Technology (FAST) Associate Professor			

[Details of activities]

Overview of achievements

S. Tsurekawa's (ST) group:

Tsurekawa's group has collaborated with Prof. Dmitri A. Molodov (RWTH Aachen University) and Prof. Pavel Lejček (Institute of Physics, Czech Academy of Sciences), who are a distinguished professor and visiting professor of IROAST, respectively, in the research field of grain boundary engineering over many years. On the occasion of Profs. D. A. Molodov and P. Lejček stayed at Kumamoto University in Nov. 2022, ST organized the IROAST workshop entitled "Fundamentals of Grain Boundary Phenomena", where four invited speakers, including Prof. D. A. Molodov and P. Lejček delivered interesting lectures. The workshop was attended by more than 50 audiences from NIMS, Tohoku University, Kyushu University, Ashikaga University in addition to from Kumamoto University, and a lively discussion took place in response to each of the presentations. During the stay of Prof. P. Lejček at KU, a new experiment concerning grain boundary segregation in a high-entropy alloy (HEA) was discussed. A part of experiment had already started with preparation of the HEA ingots on the PL side, and the ingots

supplied to ST were subjected to quantitative chemical analysis of grain boundary fracture surfaces using Auger spectroscopy.



M. Matsuda's (MM) group:

Many of functional materials, such as semiconductor, super conductor, solar cell, magnetic materials and shape memory alloys, contains numerous interfaces and domains. Functional properties are greatly affected by the interfaces and boundaries between domains. The structural and mechanical properties of nanocrystalline materials was discussed in detail with Vienna's Group (Prof. T. Waitz and Prof. C. Rentenberger) by e-mail and web meeting at twice a month. We published the paper entitled as “Structural changes of TiPt high-temperature shape memory alloys induced by high pressure torsion” to Journal of Alloys and Compounds in 2023. Also, Mitsuhiro Matsuda stayed at University of Vienna in Dec. 2022 to collaborate the research more strongly.


Publications collaborated with unit members

- [1] M. Kerber, T. Waitz, M. Matsuda, Structural changes of TiPt high-temperature shape memory alloys induced by high pressure torsion, Journal of Alloys and Compounds, 935 (2023) 168037.

Acquisition status of KAKENHI and other external grants

- [1] M. Matsuda: Grant-in-Aid for Scientific Research (B), “*Development of high temperature shape memory alloy based on the atomic shuffling mechanism in martensitic transformation*”, Grant Number JP20H02427 (from FY2020 to FY2023).
- [2] S. Tsurekawa: Grant-in-Aid for Scientific Research (B), “*Grain boundary – dislocation interactions under chemical and physical reaction fields associated with grain boundary segregation*”, Grant Number 20H001760 (from FY2022 to FY2025).
- [3] S. Tsurekawa: The Iron and Steel Institute of Japan Research Promotion Grant, “*Impact of grain boundary character and structure on hydrogen embrittlement of grain boundary in α -iron*” (from FY2022 to FY2023).
- [4] S. Tsurekawa: The Iron and Steel Institute of Japan (ISIJ) Research Project, “*Approach of grain boundary engineering for achieving high- permance steels*” (from FY2023 to FY2025).

FY2022 IROAST Research Cluster Activities Report

No.4-14	Structure and Dynamics of Materials Using Quantum Beams and Data-Driven Sciences			
Cluster Coordinator				
Name	Ichiro AKAI	Title	Professor	
Affiliation E-mail	Institute of Industrial Nanomaterials (IINa) Email: iakai@kumamoto-u.ac.jp			
Research Field	Advanced materials / Data science and AI			
Cluster Members				
Name	Affiliation/Title			
March de BOISSIEU	SIMaP, CNRS, Université Grenoble Alpes, France Director, IROAST Visiting Professor			
Matthieu MICOULAUT	Sorbonne Université, France Professor			
Anita ZEITLER	Department of Physics, University of Bath, UK Lecturer			
László PUSZTAI	Wigner Research Centre for Physics, Hungarian Academy of Sciences, Hungary/ IROAST Scientific Advisor, IROAST Distinguished Professor			
Alexei KUZMIN	Laboratory of Materials Morphology and Structure Investigations, Institute of Solid State Physics, University of Latvia, Riga, Latvia Head of Laboratory			
Masaru ANIYA	FAST, Kumamoto University Professor			
Masahiro HARA	FAST, Kumamoto University Associate Professor			
Yoichi NAKAJIMA	FAST, Kumamoto University Associate Professor			
Shinya HOSOKAWA	IINa, Kumamoto University Project Professor			

[Details of activities]

1. Research outline and its perspective

The aim of this research group is to investigate structure and dynamics of materials using quantum beam facilities in combination with data-driven sciences and computer simulations. Recent developments of quantum beam facilities, such as synchrotron radiation, x-ray free electron laser, and intense neutron sources, lead remarkable progresses in the quality of experimental data. In conjunction with them, new varieties of the data sets appear, such as two-dimensional images etc. and the corresponding data volumes explosively increase. The present

task for researchers is how to extract scientifically valuable information from the experimental data of huge size in quantity but of still insufficient in quality. In this research unit, thus, we carry out state-of-art experiments such as scattering and imaging using quantum beam facilities, and analyze the data using, e.g., Inverse problem, Bayesian inference with Metropolis' algorithm (reverse Monte Carlo modeling) and some others. Furthermore, the data-driven science such as Sparse modeling is a very promising tool for handling the data. To support the experimental results, first principles computer simulations are also indispensable.

2. Research progress and results in the fiscal year

Owing to the covid-19 pandemic problem, our activities were still limited. However, the situations became gradually improved. For example, Professor Pusztai safely visited IROAST in September for discussing with the cluster members in Kumamoto University (See photograph below left.). By using internet connections, the cluster members discussed each other about scientific projects. As a result, four internationally coauthoring papers in the research cluster were published in journals. A new collaboration started with an Italian group, Prof. Di Cicco of University of Camerino on the developments of analytical methods for synchrotron radiation data. We carried out an international symposium at Kumamoto University in September on site, and some of the members visited them in December (See photograph below right). More importantly, two young Japanese collaborators promoted to be post-doc researchers in other universities from April 2023.

Professor Akai organized an educational program on the data science for doctoral students at Kumamoto University, other universities, and industrial company members to educate the Bayesian inference, Sparse modeling, and so on.



(Left) Prof. L. Pusztai at IROAST on 1st of September. (Right) Group photograph at University of Camerino.

3. Research plan for the next year

We expect that the pandemic will be fully calmed down, some of cluster members can be gathered in some international meetings. One of them is organized by Professor Pusztai at Budapest, Hungary based on our demand. Professor Akai and some colleague will visit University of Camerino again in July. Such face-to-face communications will make a significant progress for international collaborations of the cluster members as well as young students

collaborated with us.

4. List of awards, grants, and patents, if any.

Grant:


- 1) JST CREST, I. Akai, 10,950,000 JPY
- 2) JSPS Grant-in-Aid for Scientific Research (C): M. Aniya, 1,300,000 JPY
- 3) Anritsu Corporation: M. Hara, 2,100,000 JPY
- 4) JSPS Grant-in-Aid for Scientific Research (B): Y. Nakajima, 7,200,000 JPY
- 5) JSPS Grant-in-Aid for Transformative Research Areas (A): S. Hosokawa, 3,000,000 JPY
- 6) JSPS Grant-in-Aid for Scientific Research (C): S. Hosokawa, 1,900,000 JPY

5. List of journal papers published between April 2022 and March 2023

- 1) R. Murakami, M. Mizumaki, I. Akai, and H. Shouno, Inverse estimation of parameters for the magnetic domain via dynamics matching using visual-perceptive similarity, *STAM: Method* **2**, 139 (2022).
- 2) S. Kashiwamura, S. Katakami, R. Yamagami, K. Iwamitsu, H. Kumazoe, K. Nagata, T. Okajima, I. Akai, and M. Okada, Bayesian Spectral Deconvolution of X-Ray Absorption Near Edge Structure Discriminating High- and Low-Energy Domain, *Journal of Physical Society of Japan* **91**, 074009 (2022).
- 3) N. Bisbrouck, M. Micoulaut, J.-M. Delaye, S. Gin, F. Angeli, Structure-property relationship and chemical durability of magnesium-containing borosilicate glasses: insight from topological constraints, *NPJ Materials Degradation* **6**, 58 (2022).
- 4) H. Flores-Ruiz and M. Micoulaut, Crucial Role of S₈-Rings in Structural, Relaxation, Vibrational and Electronic Properties of Liquid Sulfur close to the lambda Transition, *Journal of Chemical Physics* **157**, 054507 (2022).
- 5) M. Micoulaut, I Pethes, P. Jovari, L. Pusztai, M. Krbal, T. Wagner, V. Prokop, S. Michalik, K. Ikeda, I. Kaban, Structural Properties of Chalcogenide Glasses and the Isocoordination Rule: Disentangling Effects from Chemistry and Network Topology, *Physical Review B* **106**, 014206 (2022).
- 6) L. Gammond, R. Mendes Da Silva, A. Zeidler, H. Mohammadi, R. E. Youngman, B. G. Aitken, P. Florian, D. R. Neuville, L. Hennet, H. E. Fischer, A. C. Hannon, C. J. Benmore, and P. S. Salmon, Structure and related properties of amorphous magnesium aluminosilicates, *Physical Review Materials*. **6**, 125603 (2022)
- 7) H. Mohammadi, R. Mendes Da Silva, A. Zeidler, L. V. D. Gammond, F. Gehlhaar, M. de Oliveira Jr, H. Damasceno, H. Eckert, R. E. Youngman, B. G. Aitken, H. E. Fischer, H. Kohlmann, L. Cormier, C. J. Benmore, and P. S. Salmon, Structure of diopside, enstatite and magnesium aluminosilicate glasses: A joint approach using neutron and x-ray diffraction and solid-state NMR, *Journal of Chemical Physics* **157**, 214503 (2022).
- 8) I. Bakó, L. Pusztai, and S. Pothoczki, Topological descriptors and Laplace spectra in simple hydrogen bonded systems, *Journal of Molecular Liquids* **363**, 119860 (2022).
- 9) S. Pothoczki and L. Pusztai, On the Temperature- and Pressure-Dependent Structure of Liquid Phosphorus: A Reverse Monte Carlo Study; *Physica Status Solidi (b)* **259**, 2200082 (2022).
- 10) A. Smekhova, A. Kuzmin, K. Siemensmeyer, R. Abrudan, U. Reinholz, A. Guilherme Buzanich, M. Schneider, G. Laplanche, and K. V. Yusenko, Inner relaxations in equiatomic single-phase high-entropy cantor alloy, *Journal of Alloys and Compounds* **920**, 165999 (2022).
- 11) G. Bakradze and A. Kuzmin, Octahedral Tilting in Homologous Perovskite Series CaMoO₃-SrMoO₃-BaMoO₃ Probed by Temperature-Dependent EXAFS Spectroscopy,

- Materials* **15**, 7619 (2022).
- 12) M. Aniya, Correlating the Annealing Temperature Dependence of the Structural Inhomogeneity and the Diffusion in Zr-Ti-Cu-Ni-Be Glassy System, *Solid State Phenomena* **330**, 11 (2022).
 - 13) M. Aniya and M. Ikeda, Network Relaxation and Cooperativity in Ion Conducting Polymers PEO-Li: An Analysis Based on the BSCNF Model, *Materials Science Forum* **1059**, 129 (2022).
 - 14) H. Noda and M. Aniya, Optical Dielectric Constant and Electronegativity Difference in ANB8-N Type Binary Compounds, *Key Engineering Materials* **927**, 167 (2022).
 - 15) M. Ikeda and M. Aniya, An Extended Theory of Vacancy Formation and its Application to Ionic Conduction in the Intrinsic and Extrinsic Regions, *Philosophical Magazine* **103**, 101 (2023).
 - 16) K. Oka, S. Tateno, Y. Kuwayama, K. Hirose, Y. Nakajima, K. Umemoto, N. Tsujino, and S. I. Kawaguchi, A cotunnite-type new high-pressure phase of Fe₂S, *American Mineralogist* **107**, 1249 (2022).
 - 17) T. Hasegawa, M. Inui, T. Onimaru, Y. Kajihara, S. Hosokawa, Y. Nakajima, K. Matsuda, T. Takabatake, S. Hiroi, H. Uchiyama, and S. Tsutsui, Phonon dispersion curves in the type-I crystalline and molten clathrate compound Eu₈Ga₁₆Ge₃₀, *Journal of Physics: Condensed Matter* **35**, 114002 (2023).
 - 18) S. Hosokawa, J.-F. Bézar, N. Boudet, W.-C. Pilgrim, L. Pusztai, S. Hiroi, S. Kohara, H. Kato, H. E. Fischer, A. Zeidler, Relationship between atomic structure and excellent glass forming ability in Pd_{42.5}Ni_{17.5}Cu₃₀P₂₀ metallic glass, *Journal of Non-Crystalline Solids* **569**, 121868 (2022).
 - 19) W.-C. Pilgrim, J. R. Stellhorn, B. D. Klee, J. L. Vasco, B. Paulus, A. Zeidler, S. Hosokawa, S. Hayakawa, and S. Dehnen, Structure Determination in a new Class of Amorphous Cluster Compounds with Extreme Nonlinear Optical Properties, *Journal of Physical Society of Japan* **91**, 091004 (2022).

FY2022 IROAST Research Cluster Activities Report

No.4-15	Nano-materials for Energy Applications and Environmental Protection			
Cluster Coordinator				
Name	Tetsuya KIDA	Title	Professor	
Affiliation E-mail	Faculty of Advanced Science and Technology (FAST) Email: tetsuya@kumamoto-u.ac.jp			
Research Field	Advanced materials			
Cluster Members				
Name	Affiliation/Title			
Armando T. QUITAIN	Center for International Education, Kumamoto University/ Professor			
Maria Jose COCERO	Chemical Engineering & Environmental Technology, Universidad de Valladolid Spain/ Professor			
Yusuke INOMATA	Department of Applied Chemistry & Biochemistry, Faculty of Advanced Science and Technology, Kumamoto University/ Assistant Professor			

[Details of activities]

1. Research outline and its perspective

Our research projects are divided into four categories:

- Synthesis of colloidal quantum dots for optical applications.

Semiconductor nanocrystals called quantum dots (QDs) are expected to be used as phosphors and display materials due to their advantages such as sharp luminescence and high quantum yield (>50%). We have been studying the development of new QDs and their applications. Recently, we have focused on the extremely high luminescence efficiency (100%) of perovskite QDs with a composition of CsPbX₃ (X = Cl, Br, I). Furthermore, we discovered that the coexistence of these stabilized perovskite QDs and photochromic (PC) molecules in a solvent can control the on/off of fluorescence upon photo stimulation. We are currently exploring the application of this organic-inorganic hybrid to optical memory.

- Synthesis of oxide nanomaterials for gas sensing.

In recent years, the need for gas sensors has increased as sensors that detect environmental pollutant gases such as CO₂, NO_x, and SO_x have been put to practical use. There are several types of gas sensors, among which semiconductor sensors and solid electrolyte sensors are compact, inexpensive, and highly sensitive sensors. If materials and structures are optimized from the viewpoint of materials science and catalytic chemistry, they can detect various gases with high sensitivity. Our objective is to establish design guidelines for gas sensors that can detect chemical substances at low ppm concentrations as a new detection technology that enables continuous measurements.

- Electrochemical applications of proton/electron conducting graphene oxide membranes.

A hydrogen energy society is just around the corner, with the nationwide development of hydrogen stations and the commercialization of fuel cell vehicles. In this study, we attempted to

produce hydrogen from alcohol using a completely new hydrogen separation membrane based on an electrochemical mechanism, rather than a conventional separation membrane using porous materials. If ethanol derived from biomass can be fed to the electrochemical hydrogen permeation membrane and hydrogen can be produced by the natural oxidation of ethanol, it would be a significant carbon-neutral technology.

- Catalytic conversion of biomass into valuable compounds.

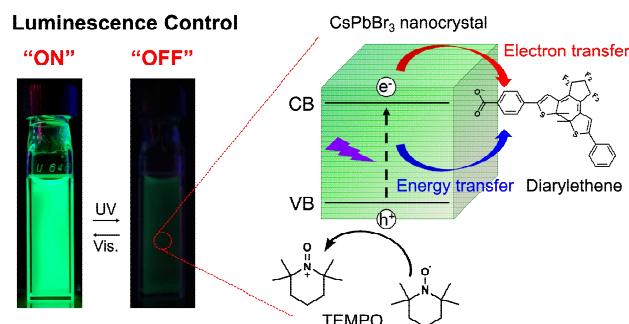
The objective is to produce value-added organic compounds from biomass containing cellulose, protein, and lignin. Cellulose can be separated from cellulosic biomass using sodium hydroxide. Sugars from cellulosic biomass can be used to produce levulinic acid and 5-hydroxymethylfurfural (HMF), which are expected to be renewable chemicals and energy sources in the future. We are currently working on the development of carbon catalysts using graphene oxide (GO), which is obtained by exfoliating graphite sheets. We have found that GO has solid acid properties and excellent microwave absorption, which can promote the hydrolysis of cellulosic biomass to glucose under microwave irradiation. By using graphene-based catalysts, glucose derived from cellulosic biomass can be converted to levulinic acid and HMF.

2. Research progress and results in the fiscal year

The key achievements include:

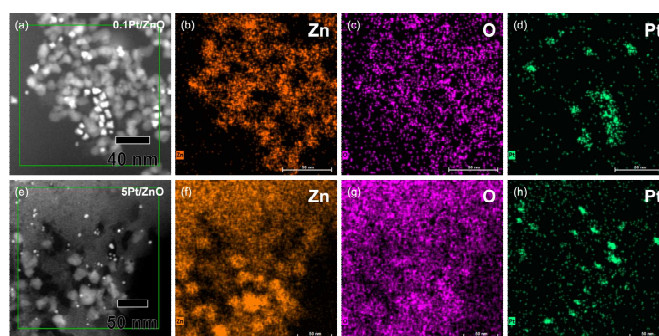
- On/Off switching of photoemission from perovskite quantum dots, CsPbX₃ (X = Cl, Br, I) by coupling with photochromic diarylethene molecules.

By suppressing electron transfer to diarylethene using TEMPO free radicals, stable switching of PL emission from QDs was successfully achieved.



- Development of highly-sensitive gas sensor for volatile organic compounds (VOCs).

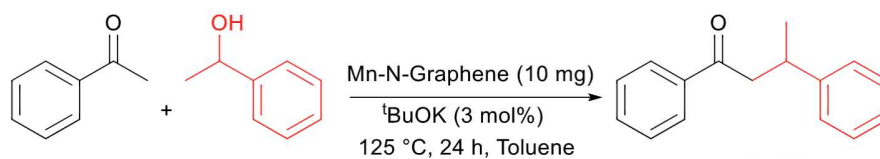
High Pt-loaded ZnO nanocrystals showed excellent sensor response to ethanol, acetone, and toluene at ppm concentrations. The detection mechanism was analyzed by in-situ DRIFTS measurements.



- Development of GO-based heterogeneous manganese catalysts for the C- and N-alkylation

of ketones.

The GO catalyst with Mn showed good activity for the conversion of ketones. This reaction could be applied to the conversion of biomass into valuable chemicals.



3. Research plan for the next year

- Synthesis of stable metal oxide coated quantum dots for energy applications.
- Analysis of gas sensing mechanism of oxide nanomaterials by operando measurements.
- Development of hydrogen separation membranes based on super proton and electron conductive graphene oxide membranes.
- Design of active catalysts for hydrogenation of biomass to produce biofuels.

4. List of grants

- MEXT/JSPS KAKENHI Grant-in-Aid for Scientific Research (B), “ON/OFF Emission Switching of Perovskite Quantum Dots”, 2020.4~2024.3, 17,680,000-yen, PI: Tetsuya KIDA
- MEXT/JSPS KAKENHI Fund for the Promotion of Joint International Research (Fostering Joint International Research (B)), “Design of highly sensitive gas recognition interfaces using 1D/2D nanomaterials”, 2020.11~2025.3, 18,720,000-yen, PI: Tetsuya KIDA
- JSPS Bilateral joint research project (open partnership with Thai), “Biomass conversion into value-added compounds using nanocarbon-based catalysts”, 2021.4~2023.3, 3,900,000-yen, PI: Tetsuya KIDA
- JSPS Bilateral joint research project (LIPI Indonesia), “Development of electrochemical devices and membrane reactors based on proton conducting carbon nanosheet membranes”, 2022.4~2024.3, 3,900,000-yen, PI: Tetsuya KIDA

5. List of journal papers published between April 2022 and March 2023

- (1) M. Ashraf, M.S. Ahmad, Y. Inomata, N. Ullah, M.N. Tahir, T. Kida, Transition metal nanoparticles as nanocatalysts for Suzuki, Heck and Sonogashira cross-coupling reactions, *Coordination Chemistry Reviews*, 476, 214928 (2023).
- (2) S. Watanabe, T. Hayashida, M. Iwai, Y. Inomata, M. Kunitake, T. Kida, Single Crystallization of Cs₄PbBr₆ Perovskite from Supersaturated Organic Solutions Optimized Through Solubility Studies, *ACS Omega*, 8, 2455–2461 (2023).
- (3) Y.L. Kam, J.K.C.N. Agutaya, A.T. Quitain, Y. Ogasawara, M. Sasaki, M.K. Lam, S. Yusup, S. Assabumrungrat, T. Kida, In-situ transesterification of microalgae using carbon-based catalyst under pulsed microwave irradiation, *Biomass and Bioenergy* 168, 106662 (2023).
- (4) Y. Akaishi, A. Mokhtar, M. Shimoyoshi, T. Nohara, Y. Inomata, D. Kosumi, T. Fukaminato, T. Kida, Light-Stimulated Luminescence Control of Lead Halide-Based Perovskite Nanocrystals Coupled with Photochromic Molecules via Electron and Energy Transfer, *Small*, 18, 2201046 (2022).
- (5) P. Nuket, Y. Akaishi, G. Yoshimura, T. Kida, P. Vas-Umnuay, In-situ TiO₂-Coated CsPbBr₃ quantum dots with enhanced stability, photoluminescence quantum yields, and charge transport properties, *Ceramics International*, 48, 32504-32512 (2022).

- (6) T. Shinkai, K. Masumoto, M. Iwai, Y. Inomata, T. Kida, Study on Sensing Mechanism of Volatile Organic Compounds Using Pt-Loaded ZnO Nanocrystals, *Sensors*, 22, 6277 (2022).
- (7) M.S. Ahmad, Y. Inomata, T. Kida, Heterogenized manganese catalyst for C-, and N-alkylation of ketones and amines with alcohols by pyrolysis of molecularly defined complexes, *Molecular Catalysis*, 526, 112390 (2022).
- (8) A.S.A. Fauzi, N.L. Hamidah, S. Kitamura, T. Kodama, K. Sonda, G.K. Putri, T. Shinkai, M. S. Ahmad, Y. Inomata, A. T. Quitain, T. Kida. Electrochemical Detection of Ethanol in Air Using Graphene Oxide Nanosheets Combined with Au-WO₃, *Sensors*, 22, 3194 (2022).