TOKYO
METROPOLITAN
UNIVERSITY

Faculty of Environmental Sciences
Department of Applied Chemistry for Environment

Graduate School of Environmental Sciences
Department of Applied Chemistry for Environment

Annual Report 2021

Index

Reports from Research Groups

Kawakami Laboratory

■**Members**
Hiroyoshi KAWAKAMI
Professor / Dr. Eng.
Polymer Chemistry, Functional Polymers, Nanofiber Engineering, Biomaterials, Epigenetics Engineering, Cell Engineering
Rm. 9-638, +81-42-677-1111 Ext. 4972
kawakami-hiroyoshi@tmu.ac.jp

Masafumi YAMATO
Associate Professor / Dr. Eng.
Polymer Science, Magneto-Science
Rm. 9-137, +81-42-677-1111 Ext. 4837
yamato-masafumi@tmu.ac.jp

Kiyoshi SATO
Associate Professor / Dr. Eng.
Synthetic Organic Chemistry, Molecular Recognition, Heterocyclic Chemistry, Physical Organic Chemistry
Rm. 9-349, +81-42-677-1111 Ext. 4886
sato-kiyoshi@tmu.ac.jp

Manabu TANAKA
Associate Professor / Dr. Eng.
Polymer Chemistry, Polymer Energy Materials, Fuel Cells, Secondary Batteries, Nanofibers, Polymer Membranes
Rm. 9-639, +81-42-677-1111 Ext. 4586
tanaka-manabu@tmu.ac.jp

Toyotaka NAKAE
Research Assistant Professor / Dr. Sci.
Organometalic Chemistry, Coordination Chemistry, Inorganic Chemistry
Rm. 9-349, +81-42-677-1111 Ext. 4886
nakae-toyotaka@tmu.ac.jp

Doctor's course - 2
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■**Outlines of the Research**

1. Study of Functional Polymer Membrane
Hiroyoshi KAWAKAMI, Masafumi YAMATO

Membrane-based gas separations have tremendous potential as energy-efficient alternatives or removal material of greenhouse gasses, such as carbon dioxide (CO_2). Recently, we have reported that novel composite membranes composed of the fluorinated polyimide or polymers of intrinsic microporosity (PIM) and surface-modified silica nanoparticles exhibit high gas permeability and selectivity.

In this year, we evaluated the gas permeation characteristics of PIM-1 and silica particle / PIM-1 composite membranes at the exhaust gas temperature of thermal power plants. It was clarified that the gas permeability coefficient of PIM-1 significantly decreased above 80 ° C. On the other hand, the silica particle / PIM-1 composite membrane also showed a tendency to decrease the gas permeability coefficient at high temperature due to the temperature characteristics of PIM-1, but the gas permeability coefficient was significantly improved by the addition of particles.

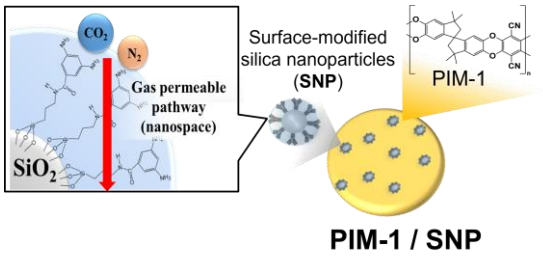


Figure 1. Schematic drawing of nanoparticle/PIM-1 composite membrane.

2. Study of Polymer Electrolyte Membrane
Hiroyoshi KAWAKAMI, Manabu TANAKA, Toyotaka NAKAE

Polymer electrolyte fuel cells have attracted much attention as clean and sustainable energy systems. We have reported composite polymer electrolyte membranes based on phytic acid (Phy)-doped polybenzimidazole nanofibers (PBINF) showed outstanding fuel cell performances under low relative humidity conditions.

In this year, we synthesized sulfonated polymers veering high ion exchange capacities. The novel polymer composite membranes containing proton conductive acid-base blend polymer nanofibers showed improved proton conductivity, especially at low relative humidity. Proton conductivity and gas barrier properties at high temperatures above 100°C was were evaluated for future fuel cell operation.

New study on water electrolysis and metal-air secondary batteries using anion exchange membranes were also carried out.

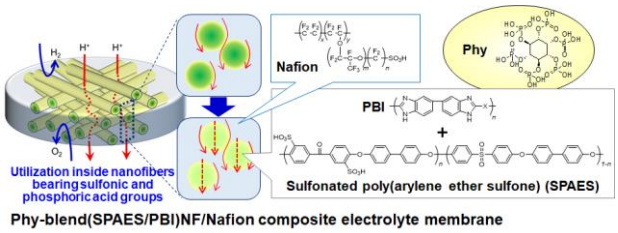


Figure 2. Novel proton conductive blend nanofiber composite membrane.

3. Study of Electrospun Nanofibers
Hiroyoshi KAWAKAMI, Manabu TANAKA

Recently, nano-scale fibers prepared through an electrically charged jet of polymer solution/melt (electrospinning) have received a lot of attention. Nanofibers have several inherent characteristics including high surface area, unique optical and physicochemical properties originated from the nano-size, and alignment of polymer chains in the nanofibers. The diameter of nanofiber is one of the most important factors to effect on such unique characteristics. Ultrafine nanofibers with their diameters less than 50 nm were also obtained.

In this year, we focused on the development of polymer nanofiber composite membranes for all solid state secondary batteries. The novel polymer composite membranes containing polar crystalline poly(vinylidene fluoride-co-trifluoro ethylene) nanofibers showed good secondary battery performances at low temperatures by modifying the interfaces between the electrolyte and electrodes.

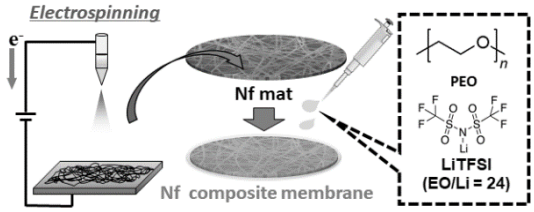


Figure 3. Schematic illustration of the lithium ion battery using the lithium ion conductive polymer nanofiber composite membrane.

4. Design of Multi-electron Redox Catalysts

Hiroyoshi KAWAKAMI, Kiyoshi SATO, Toyotaka NAKAE

Native metallo-enzymes facilitate various types of chemical reactions under mild conditions in water. Thus, an artificial metal complex as a bioinspired metallo-enzyme has application potential for wide field of chemistry such as energy chemistry and medicinal chemistry.

In this year, we have prepared tandem catalyst-modified electrodes fabricated by drop-cast deposition of metalloporphyrins bearing phenolic OH substituents spatially arranged around the metal center onto copper nanocrystals. The tandem catalyst-modified electrodes improve the C2/C1 product selectivity due to persistent elevation of the local CO concentration on Cu surface for promoting C-C coupling. Further improvement of the catalytic activity and the product selectivity is under investigation

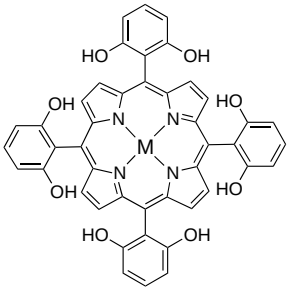


Figure 4. Proton-coupled multi-electron redox catalyst for electrocatalytic CO_2 reduction.

5. Epigenetics Engineering for Cancer Therapy

Hiroyoshi KAWAKAMI, Kiyoshi SATO

The development and maintenance of an organism is orchestrated by a set of chemical reactions that switch parts of the genome off and on at strategic times and locations. Epigenetics is the study of these reactions and the factors that influence them.

In this year, we have prepared novel epigenetics control (EpC) carriers for a novel therapeutic treatment of cancer. The EpC carriers that transport three types of epigenetic agents simultaneously into a target cell successfully mediate the apoptosis induction, cellular senescence induction, and epithelial-to-mesenchymal transition (EMT) suppression in HCT116 human colorectal carcinoma cells by the combined effect of the carrier-encapsulated epigenetic drugs.

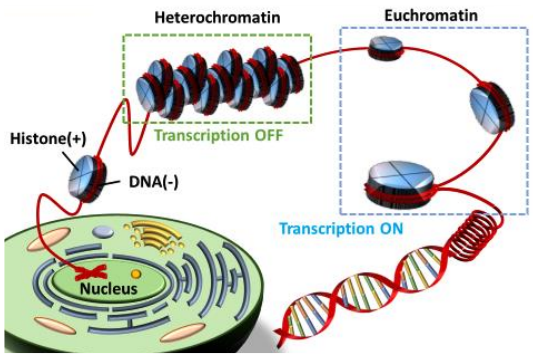


Figure 5. Epigenetic gene expression control by chromatin conformations.

6. Suppression of Cellular Senescence

Hiroyoshi KAWAKAMI, Kiyoshi SATO,

While cellular senescence acts as a tumor suppressor, the accumulation of senescent cells causes diabetes and Alzheimer's disease, and also develop a senescence-associated secretory phenotype (SASP) that can adversely affect the behavior of neighboring cells. Cellular senescence is also a major factor in the deterioration of cell quality during *in vitro* cell expansion of multifunctional cells for regenerative medicine and cell therapy. Therefore, suppression of cellular senescence of stem cells and immune cells is one of the most important issues for regenerative medicine and cell therapy.

In this year, we investigated the suppression of replicative senescence of mesenchymal stem cells and NK cells by mitophagy-induced liposome nanocarriers (M-NC). The administration of M-NC was found to restore the cell proliferation ability and cell function by removing dysfunctional mitochondria from senescent cells *via* mitophagy reactivation. Moreover, M-NC can act not only suppress cellular senescence but also rejuvenate long-term cultured cells from the senescence state. Thus, M-NC will provide new strategies for the *ex vivo* cell expansion of the cell source for regenerative medicine and cell therapy.

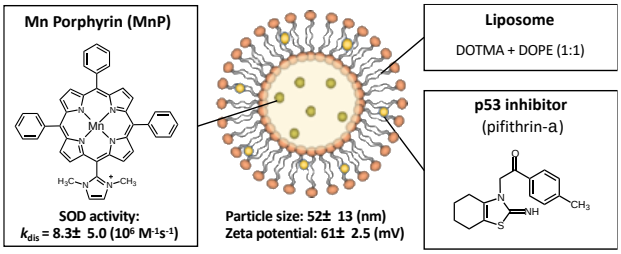


Figure 6. Mitophagy-induced liposomal nanocarrier.

7. Processing of feeble magnetic materials under a magnetic field

Masafumi YAMATO

Controls of higher-order structure of feeble magnetic materials by using a magnetic field have been studied in order to improve some properties and to reveal new functions of the materials.

In this year, we discovered a lyotropic liquid crystal consisting of nanosheets and ionic liquids. The formation of the liquid

crystal significantly improved the magnetic field response. We also succeeded in immobilizing the liquid crystal structure by in-situ polymerization after adding the monomer.

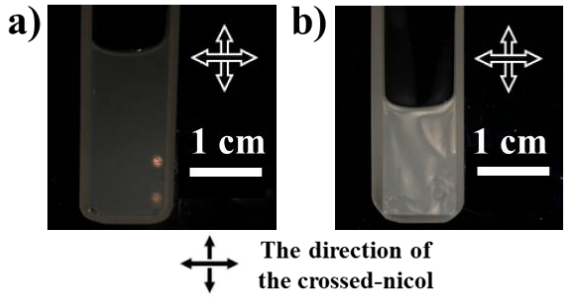


Figure 7. Photo images of (a) the transparent layer and (b) the turbid layer of ionic liquid dispersion of montmorillonite under cross-Nicol condition.

■Papers with Peer Review

1. Takahiro Ogura, Kazuto Suzuki, Manabu Tanaka, Hiroyoshi Kawakami, "Fabrication and Characterizations of Polymer Electrolyte Composite Membranes Consisted of Polymer Nanofiber Framework Bearing Connected Proton Conductive Pathways", Journal of Photopolymer Science and Technology, 34, 5, 463-468 (2021).
2. Takeru Wakiya, Manabu Tanaka, Hiroyoshi Kawakami, "Fabrication and Electrolyte Characterizations of Nanofiber Framework-Based Polymer Composite Membranes with Continuous Proton Conductive Pathways", Membranes, 11, 90 (2021).
3. Shun Nakazawa, Yu Matsuda, Mitsuki Ochiai, Yuta Inafune, Masafumi Yamato, Manabu Tanaka, Hiroyoshi Kawakami, "Enhancing Lithium Ion Conductivity and All-Solid-State Secondary Battery Performance in Polymer Composite Electrolyte Membranes with β-Crystalline-rich Poly(vinylidene fluoride) Nanofibers", Electrochimica Acta, 394, 139114 (2021).
4. Manjit Singh Grewal, Manabu Tanaka, Hiroyoshi Kawakami, Solvated Ionic-Liquid Incorporated Soft Flexible Cross-Linked Network Polymer Electrolytes for Safer Lithium Ion Secondary Batteries, Macromolecular Chemistry and Physics, in press (2022).
5. Shiori Higashi, Masafumi Yamato, Hiroyoshi Kawakami "Effect of Phase Separation due to Solvent Evaporation on Particle Aggregation in the Skin Layer of the Gas Separation Membrane", Journal of Photopolymer Science and Technology, 34, 449-456 (2021).
6. Takeru Yamazaki, Kohe Arima, Riku Kubota, Kiyoshi Sato, Hiroyoshi Kawakami, "Preparation of Mitochondria- and Epigenetics-Targeting Nanoparticles for Suppression of Cancer Metastasis", Part. Part. Syst. Charact., 38 (8), 2100003 (2021).
7. Takahiro Miyazaki, Kazuma Komine, Takashi Nakaoji, Kohki Takahashi and Masafumi Yamato, Magnetic birefringence of montmorillonite dispersion, The Japanese Journal of Applied Physics, Accepted January 2022.
8. Urano Chisato, Masatoshi Onuki, Yuuta Uchida, Risa Suzuki, Kiyoshi Sato, Dai Masui, Motowo Yamaguchi, Takamichi Yamagishi, "Asymmetric allylic substitution by chiral palladium catalysts: Which is more reactive, major pi-allyl Pd(II) species or minor pi-allyl species?", Molecular Catalysis, 499, 111221 (2021).
9. Bofan Zhang, Mutian Zhang, Liang Zhang, Paul A. Bingham, Manabu Tanaka, Wen Li, Shiro Kubuki, "BiOBr/MoS_2 catalyst as heterogenous peroxymonosulfate activator toward organic pollutant removal: Energy band alignment and mechanism insight", Journal of Colloid and Interface Science, 594, 635-649 (2021)
10. Shogo Mamada, Tatsuya Ohta, Masafumi Yamato, "The elasticity and the piezoelectricity of thick composites of silicone rubber matrix and aligned piezoelectric ceramic particles", Plastics Rubber and Composites, 50, 455-463 (2021).
11. Kazushi Enomoto, Kotaro Takeda, Naoto Iwata, Kiyohiro Adachi, Tomoka Kikitsu, Yasuhiro Ishida, Daisuke Hashizume, Manabu Tanaka, Hiroyoshi Kawakami, Yong-Jin Pu, "Colloidal CdS Quantum Dot Fibers Prepared by Electrospinning of Their Wet Gel for Quantum Nanowires", *ACS Applied Nano Materials*, accepted

■Books

1. Kazuma Komine, Masafumi Yamana, "NMR Analysis of organic adsorption on clay", Technical Information Institute, September 2021.
2. Manabu Tanaka, Hiroyoshi Kawakami, "Development of Polymer Nanofiber-based Electrolyte Membranes for PEFCs", Electrochemistry, in press (2021)
3. Masafumi Yamato, Hiroyoshi Kawakami, " Development of polymeric gas separation membrane complexed with surface-modified nanoparticles ", The latest technology for CO_2 separation, recovery, and storage, NTS(Tokyo, Japan), in press. (in Japanese)

■Invited Lectures

1. Hiroyoshi Kawakami, Development of electrolyte membranes for fuel cells required after 2030, Special lecture at Iwate University (Morioka), October 2021, (in Japanese).
2. Masafumi Yamato, Thermal and magnetic properties of polymer, *2021 Basic seminar of polymer science for young engineers*, Nov. 2021, Online (in Japanese).
3. Hiroyoshi Kawakami, Scientific (chemical) approach against COVID-19 in the present and future, Special lecture in Miyako festival at Tokyo Metropolitan University, November 2021, Online (in Japanese).
4. Hiroyoshi Kawakami, Cell rejuvenation by nanocarrier, Cosme Tech 2022 Tokyo (Tokyo), January 2022 (in Japanese).
5. Hiroyoshi Kawakami, Development of ultra-high CO_2 permeable separation membrane required for CCS and CCU, SPSJ, January 2022, Online (in Japanese).
6. Hiroyoshi Kawakami, Fuel cell technology development roadmap, 7th FC-Cubic symposium, March 2022, Online (in Japanese).
7. Hiroyoshi Kawakami, Development of innovative ultra-high CO_2 permeable separation membrane required by CCUS, SPSJ, March 2022, Online (in Japanese).
8. Hiroyoshi Kawakami, Development of ultra-high CO_2 permeable separation membrane required by CCUS, The Membrane Society of Japan,, March 2022, Online (in Japanese).

■Academic Meeting

1. Shiori Higashi, Masafumi Yamato, Hiroyoshi Kawakami,

Preparation of asymmetric membranes containing surface-modified silica nanoparticles and the gas permeation properties, 70th SPSI Annual Meeting (Online Virtual Meeting), 1Pa045, May 2021.

2. Nakaoji Takashi, Masafumi Yamato, and Kawakami Hiroyoshi, Application of fluorinated hectorite / hectorite lyotropic liquid crystals to nanocomposite hydrogels, 70th SPSJ Annual meating, Online, 2F23, May 2021 (in Japanese)
3. Kazuto Suzuki, Manabu Tanaka, Hiroyoshi Kawakami, Fabrication and characterizations of acid / base blend polymer nanofiber composite membranes for high temperature and low humidity fuel cell operation, The 70th SPSJ Annual Meeting (Online), 3Pe063 May 2021 (in Japanese)
4. Yuri Nara, Manabu Tanaka, Hiroyoshi Kawawaki, Fabrication and evaluation of anion conductive polymer electrolyte membranes for water electrolysis., The 70th SPSJ Annual Meeting, 3Pb066, May 2021 (in Japanese)
5. Kazuto Suzuki, Manabu Tanaka, Hiroyoshi Kawakami, Fabrication and evaluation of polymer blend nanofiber composite membranes for wide temperature and low humidity fuel cell operation, The 28th Fuel Cell Symposium (Online), No.17 May 2021 (in Japanese)
6. Kiyioshi Sato, Keisuke Ashiba, Hiroyoshi Kawakami, Mitophagy Reactivation and Rejuvenation of Senescent Stem Cells by Liposome Nano Carriers, Joint Meeting of the 74th Annual Meeting of Society for Free Radical Research JAPAN and the 21st Nitric Oxide Society of JAPAN, (Sendai International Center, Live-Web) 10043 (May, 2021). (in Japanease).
7. Nohara Yokota, Manabu Tanaka, Hiroyoshi Kawakami, Evaluation of their lithium-ion conductivity of high salt-concentrated solid polymer electrolyte membranes with nanofiber frameworks, 43th The Membrane Society of Japan, June 2021 (Online) (in Japanease)
8. Takumu Morita, Masafumi Yamato, Hiroyoshi Kawakami, Fabrication and gas permeation property of PIM-1/PIM-CTC blend membrane to improve gas., 43st annual meeting of membrane science of Japan, June 2021, E-307, (Online). (in Japanease)
9. Nana Terasoba, Manabu Tanaka, Hiroyoshi Kawakami, Fabrication and evaluation of lithium salt-containing polycarbonate-based composite electrolyte membrane composed of nanofibers with polarized crystals, 43st annual meeting of membrane science of Japan, June 2021 (Online). (in Japanease)
10. Kazuto Suzuki, Manabu Tanaka, Hiroyoshi Kawakami, Fabrication and characterization of acid-doped blend nanofiber composite membranes for high temperature and low humidity fuel cell operation, The Annual Meeting of the Society of Fiber Science and Technology (Online), 1PB208 June 2021 (in Japanese)
11. Yuri Nara, Manabu Tanaka, Hiroyoshi Kawakami. Synthesis and Electrolyte Evaluation of Anion Conductive Polymers Bearing No Heteroatoms in the Polymer Main Chains., The Annual Meeting of the society of fiber science and technology Japan, 1PA209, June 2021 (in Japanese)
12. Yuri Nara, Tanaka Manabu, Hiroyoshi Kawakami. Fabrication and Electrolyte Evaluation of Novel Anion Exchange Membranes for Water Electrolysis., The Annual Meeting of the society of fiber science and technology Japan, 2C13 June 2021 (in Japanese)
13. Takahiro Ogura, Kazuto Suzuki, Manabu Tanaka, Hiroyoshi Kawakami, Fabrication and Characterizations of Polymer Electrolyte Composite Membranes Consisted of Polymer Nanofiber Framework Bearing Connected Proton Conductive Pathways, ICPST-38 (Online), B1-11 June 2021 (in Japanese)
14. Koki Mino, Takeru Yamazaki, Keisuke Ashiba, Kiyoshi Sato, Hiroyoshi Kawakami, Mitophagy-inducing nanocarrier for functional recovery of senescent mesenchymal stem cells, The 37th Annual Meeting of the Japanese Society of Drug Delivery System (Makuhari Messe), 2-B-07, (June 2021)
15. Shiori Higashi, Masafumi Yamato, Hiroyoshi Kawakami, Effect of Phase Separation due to Solvent Evaporation on Particle Aggregation in the Skin Layer of the Gas Separation Membrane, The 38th International Conference of Photopolymer Science and Technology, (Online Virtual Meeting), B1-8, June 2021.
16. Keisuke Ashiba, Takeru Yamazaki, Kiyoshi Sato, Hiroyoshi Kawakami, Suppression senescence in mesenchymal stem cells by mitophagy-inducing liposome nanocarrier. 50th Medical macromolecular symposium (On-line), 7 (July, 2021)
17. Yokota Nohara, Manabu Tanaka, Hiroyoshi Kawakami, Fabrication and Characterizations of Solid Polymer Electrolyte in High-Salt Concentration Region for All-Solid-State Batteries, 4th G'L'owing Polymer Symposium in KANTO, July 2021 (Online).
18. Yuri Nara, Manabu Tanaka, Hiroyoshi Kawakami, Synthesis and Evaluation of Anion Conductive Polymers for Water Electrolysis Application., 4th G'L'owing Polymer Symposium in KANTO (GPS-K 2021), (Online), A20, July 2021.
19. Manabu Tanaka, Yuu Matsuda, Hiroyoshi Kawakami, Fabrication and Characterization of Lithium-Air Battery Consisted of Nanofiber Composite Electrolyte Membrane with Suppressed Water Vapor Permeability, 70th Polymer Symposium in Japan, September 2021 (Online) (in Japanease)
20. Nohara Yokota, Manabu Tanaka, Hiroyoshi Kawakami, Lithium-ion conductive characteristics of polarizable polymer nanofiber-based composite solid polymer electrolytes bearing high salt concentrations, 70th Polymer Symposium in Japan, September 2021 (Online) (in Japanease)
21. Takumi Kobayashi, Kiyoshi Sato, Hiroyoshi Kawakami, Analysis of Electrochemical CO2 Reduction Products of Metal Porphyrin-Modified Electrodes by Rotating Ring-Disk Electrode Method, Electrochemistry Autumn Meeting 2021 (Online Conference), 1A15 (September 2021).
22. Kazuma Komine, Masafumi Yamato, and Kawakami Hiroyoshi, Development of Lyotropic Liquid Crystal comprising Ionic Liquid and Clay Nanosheet., the 82th JSAP autumn Meeting, (Online Virtual Meeting), 12a-N324-9, September 2021.
23. Shuntarou Kimura, Risa Mitsuhashi, Kiyoshi Sato, Hiroyoshi Kawakami, Epigenetics control nanoparticle inducing cellular senescence for cancer cells, The 43rd

Annual Meeting of the Japanese Society for Biomaterials（Nagoya Congress Center）, JO-2H07（November 2021）

24. Koki Mino, Keisuke Ashiba, Kiyoshi Sato, Hiroyoshi Kawakami, Mitophagy-inducing nanocarriers for functional recovery of senescent mesenchymal stem cells, 59th Annual Meeting of the Japanese Society for Artificial Organs, Hilton Tokyo Bay, YP2-4 (Nov. 2021)
25. Kazuma Komine, Masafumi Yamato, and Kawakami Hiroyoshi, Magnetic orientation of Liquid Crystal comprising Clay and Ionic Liquid and its characteristics., 15th Magneto-Science Society of Japan , Online, P-06, November 2021 (in Japanese)
26. Nakaoji Takashi, Masafumi Yamato, and Kawakami Hiroyoshi, Magnetic orientation of clay using liquid crystal phase formed by nanosheets, 15th Magneto-Science Society of Japan , Online, P-05, November 2021 (in Japanese)
27. Shuntarou Kimura, Risa Mitsuhashi, Kiyoshi Sato, Hiroyoshi Kawakami, Induction of cellular senescence in cancer cells by epigenetics control carrier, The 44th Annual Meeting of the Molecular Biology Society of Japan（PACIFICO Yokohama), 3P-0562 (December 2021)
28. Haruka Nishimura, Keisuke Ashiba, Kiyoshi Sato, Hiroyoshi Kawakami, Restoration of senescent mesenchymal stem cells using mitophagy inducing nanocarriers, The 44 th Annual Meeting of the Molecular Biology Society of Japan (PACIFICO Yokohama), December 2021
29. Yokota Nohara, Manabu Tanaka, Hiroyoshi Kawakami, Polymer nanofiber-based high-salt concentration PEO composite electrolytes and their lithium ion conductivity evaluation, 62nd Battery Conference, November 2021 (in Japanease)
30. Keisuke Ashiba, Takeru Yamazaki, Koki Mino, Kiyoshi Sato, Hiroyoshi Kawakami, Rejuvenation of mesenchymal stem cells by liposome nanocarrier inducing mitophagy, TERMIS 6TH WORLD CONGRESS 2021 (On-line), 2017 (November 2021)
31. Kazuto Suzuki, Manabu Tanaka, Hiroyoshi Kawakami, Functional Nanofiber Reinforcement Layer that Assists Proton Transport under High Temperature and Low Humidity, The 62 th Battery Symposium (Hybrid), 3C03 December 2021 (in Japanese)
32. Yasutaka Kuwahara, Kazuma Komine, Hiroyoshi Kawakami, Fabrication and evaluation of proton conductive crosslinked PVA nanofibers. The 59th research Group on the Interaction between Polymer and Water and Separation Science, PB2, December 2021 (in Japanese)
33. Yuri Nara, Manabu Tanaka, Kensaku Nagawsawa, Yoshiyuki Kuroda, Shigenori Mitsushima, Hiroyoshi Kawakami, Fabrication and Water Electrolysis Evaluation of Anion Exchange Membranes with High Alkaline Stability., The 59th Symposium on the Interaction between Polymer and Water and Separation Science, PB3, December 2021
34. Kazuma Komine, Masafumi Yamato, and Kawakami Hiroyoshi, Fabrication of anisotropic ionic gel containing Clays., 93th Musashino area polymer association, Online, P14, December 2021 (in Japanese)
35. Honomi Miyashita, Masafumi Yamato, Hiroyoshi Kawakami, Higher-order structure of iPP / VGCF composite material, The 93rd Musashino district polymer social gathering, (Online Virtual Meeting), December 2021.
36. Nakaoji Takashi, Masafumi Yamato, and Kawakami Hiroyoshi, Application of liquid crystal phase formed by clay nanosheets to nanocomposite gel, 93th Musashino area polymer association, Online, P15, December 2021 (in Japanese)
37. Honomi Miyashita, Masafumi Yamato, Hiroyoshi Kawakami, Structural analysis of iPP / VGCF composites oriented by magnetic field, The Magneto-Science Society of Japan, The 29th research society, (Online Virtual Meeting), December 2021.
38. Kazuma Komine, Masafumi Yamato, and Kawakami Hiroyoshi, Magnetic orientation of ionic liquid-clay nanosheet liquid crystal., 29th Meeting of JSAP- Magneto-Science Society of Japan 2021, Online, P, December 2021 (in Japanese)
39. Nakaoji Takashi, Masafumi Yamato, and Kawakami Hiroyoshi, Magnetic field orientation of lyotropic liquid crystal consisting of different clay, 29th Meeting of JSAP-Magneto-Science Society of Japan 2021, Online, P-2A, December 2021 (in Japanese)
40. Kazuma Komine, Masafumi Yamato, and Kawakami Hiroyoshi, Fabrication of anisotropic ion gel using magnetic orientation of clay nanosheet liquid crystal., the 69th JSAP Spring Meeting, (Online Virtual Meeting), 22a-E205-12, March 2022.

■Patents

1. JP2021-185233,A “Hyperbranch polymer- or dendrimer polymer-added silica nanoparticle and composite”, (published 2021. 12. 9)
2. JP2021-24852,A “Cmposite for decompose dysfunctional mitochondria and composite for scell enescence inhibition” (published 2021. 2. 22)

■Awards

1. 43st annual meeting of membrane science of Japan, Student Award, Nana Terasoba, Manabu Tanaka, Hiroyoshi Kawakami, “Fabrication and evaluation of lithium salt-containing polycarbonate-based composite electrolyte membrane composed of nanofibers with polarized crystals”.
2. The Annual Meeting of the society of fiber science and technology Japan, Excellent Poster Award, Yuri NARA, Manabu Tanaka, Hiroyoshi Kawakami. “Synthesis and Electrolyte Evaluation of Anion Conductive Polymers Bearing No Heteroatoms in the Polymer Main Chains”.
3. The 70th SPSJ Annual Meeting, Excellent poster award, Kazuto Suzuki, Manabu Tanaka, Hiroyoshi Kawakami, “Fabrication and characterizations of acid / base blend polymer nanofiber composite membranes for high temperature and low humidity fuel cell operation”.
4. The 59th Symposium on the Interaction between Polymer and Water and Separation Science, Excellent Poster Award, Yuri Nara, Manabu TANAKA, Kensaku NAGASAWA, Yoshiyuki KURODA, Shigenori MITSUSHIMA, Hiroyoshi Kawakami, “Fabrication and Water Electrolysis Evaluation of Anion Exchange Membranes with High Alkaline Stability”.
5. The 10th Excellent Research Award of the Magneto-

Science Society of Japan, Masafumi Yamato, "Research on polymeric material control using magnetic process".

6. The 70th Polymer Symposium in Japan, Publicity Award, Manabu Tanaka, Yu Matsuda, Hiroyoshi Kawakami, “Fabrication and Characterization of Lithium-Air Battery Consisted of Nanofiber Composite Electrolyte Membrane with Suppressed Water Vapor Permeability”
7. 59th Annual Meeting of the Japanese Society for Artificial Organs, Poster Award, Koki Mino, Keisuke Ashiba, Kiyoshi Sato, Hiroyoshi Kawakami, “Mitophagy-inducing nanocarriers for functional recovery of senescent mesenchymal stem cells”.

Asayama Laboratory

■Members
Shoichiro ASAYAMA
Associate Professor / Dr. Eng.
Biomaterials, Drug Delivery System, Biomedical Polymers, Biomolecular Engineering, Biochemistry
Rm. 9-651, +81-42-677-1111 Ext. 4976
asayama-shoichiro@tmu.ac.jp

Master's course -9
Bachelor 4 -3

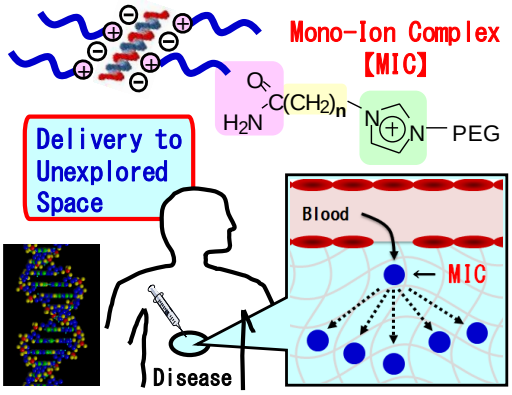
■Outlines of the Research

To improve human health and quality of life (QOL), we have designed new biomaterials. Especially, we have designed new drug delivery system (DDS) for advanced and homogeneous medicine as follows:

1. Nucleic Acid (Plasmid DNA, various RNAs) Delivery System

Shoichiro ASAYAMA

As water-soluble (liquid-phase) biomaterials, the carriers of nucleic acid as a macromolecular drug have been designed for unmet medical needs. Recently, the mono-ion complex (MIC) to make plasmid DNA (pDNA), as a gene, highly condensed has been formed for



delivery to *in vivo* unexplored space (Figure 1).

Figure 1. Delivery to *in vivo* unexplored space by the mono-ion complex (MIC).

In this year, we have synthesized diethylamino (DEA) end-modified PEG with imine spacer (DEA=PEG) to improve the formation stability of MICs and to achieve more significant *in vivo* gene expression. The DEA group is expected to stabilize the electrostatic interaction as a highly hydrophobic cationic moiety. And, an imine group has been selected as a spacer for PEG chain dissociation by hydrolysis, as well as a partial cationic moiety to be iminium ion or neutral imine at physiological pH.

2. Bioactive Substance (Zn^{2+}, protein) Delivery System

Shoichiro ASAYAMA

To give DDS carrier the ability for definitive treatment, we have designed pH-sensitive polyvinylimidazole (PVIm) derivateives as intelligent materials to change their structure and function in respons to external stimuli. Recently, Zn^{2+} delivery to liver is applied for remote control of hypoglycemic hormone (Figure 2).

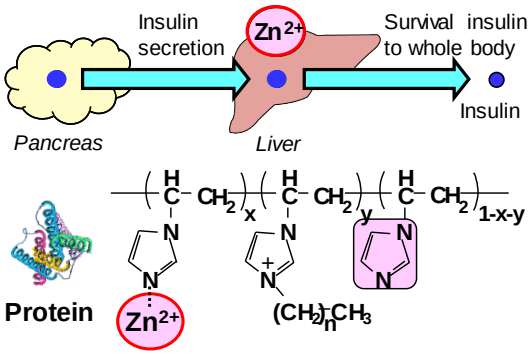


Figure 2. Remote control of hypoglycemic hormone in blood.

In this year, we have synthesized hepatocyte-specific Zn-porphyrin-carbohydrate conjugates (ZnP-Am-Lac). These molecules have a porphyrin backbone to be capable of stably coordinating Zn^{2+} *in vivo* and have four ß-galactose residues, which allows it to be recognized by the asialoglycoprotein receptor (ASGP-R) expressed on hepatocytes in a multivalent manner, and to be efficiently uptaken by hepatocytes. The inhibition experiment of the intracellular uptake of ZnP-Am-Lac proves that the hepatocyte-specific recognition via ASGP-R is attributed to the nonionic amide spacer between ZnP and Lac. Furthermore, the resulting Zn^{2+} delivery by the ZnP-Am-Lac has suppressed insulin degradation in human hepatocytes.

3. Biomaterials with Funtional Surface

Shoichiro ASAYAMA

As water-insoluble (splid-phase) biomaterials, to design medical devices working *in vivo* or *ex vivo* with efficient biocompatibility, we have recently applied cholesterol end-modified poly(ethylene glycol), that is, Chol-PEG, as DDS carrier to the non-covalent modification of solid surface (Figure 3).

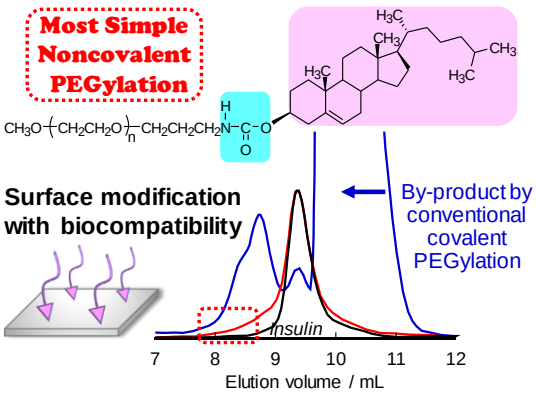


Figure 3. Development of novel bio-function by Chol-PEG.

In this year, manganese or iron tetrakis(4-carboxyphenyl)porphyrin (Mn, Fe-TCPP) and methylated poly(1-vinylimidazole) (PVIm-Me) or octylated poly(1-vinylimidazole) (PVIm-Oc) were modified on the dialysis membrane by a non-covalent bond using the layer-by-layer method. Thus, we have prepared a functional hemodialysis membrane with catalase pseudo-active center on the surface for a unique device that can decompose hydrogen peroxide during hemodialysis.

■Papers with Peer Review

1. Akito Endo and Shoichiro Asayama, Hepatocyte-specific co-delivery of zinc ions and plasmid DNA by lactosylated poly(1-vinylimidazole) for suppression of insulin receptor internalization, *Pharmaceutics*, 13, 2084-2093 (2021).
2. Haibo Qiao and Shoichiro Asayama, Guanidinopropyl end-modified poly(ethylene glycol) to form highly compact plasmid DNA mono-ion complexes by thermal treatment, *Polymers for Advanced Technologies*, 33, 484-491 (2022).

■Reviews

1. Shoichiro Asayama, Noncovalent PEGylation of protein and plasmid DNA fo the delivery system, Feature Articles “Biomaterials for Good Health and Well-Being”, *Journal of Japanese Society for Biomaterials*, Vol. 39, No. 4, 222-227 (2021).

■Academic Meeting

See the annual report in Japanese (18 articles)

■Patents

See the annual report in Japanese (1 patent).

Kubo Laboratory

■**Members**
Yuji Kubo
Professor /Dr. Eng.
Organic Chemistry, Supramolecular Chemistry, Functional Dye
Room: 9-448 TEL: +81-42-677-3134
e-mail: yujik@tmu.ac.jp

Masato Ito
Assistant Professor /Dr. Sci.
Structural Organic Chemistry, Main-group Chemistry, Functional Dye
room:9-438 TEL: +81-42-677-1111 (Ext. 4941)
e-mail: mito@tmu.ac.jp

Doctor's course -2
Master's course -9
Bachelor -5

■**Outlines of the Research**

1. Organic room-temperature phosphorescence materials
Yuji Kubo

Abstract
Considering low-cost, abundant resources and low environmental pollution compared to precious metal-containing inorganic materials, organic room-temperature phosphorescence (RTP) materials with improvement of intersystem crossing (ISC) channel and minimization of vibration-based and oxygen-mediated quenching have attracted considerable attention. In this context, boronate particles prepared by dehydration reaction of benzene-1,4-diboronic acid with pentaerythritol, which showed RTP behavior with a green afterglow in water. The long-lived lifetime has motivated us to develop afterglow materials for application in chemseonesors.

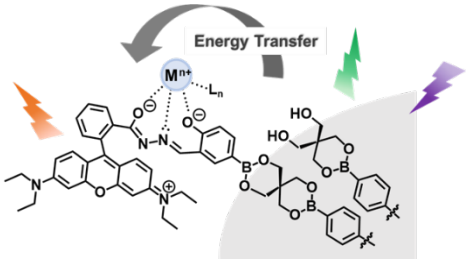


Figure 1. Metal ion-responsive afterglow martials.

2. Arylselanyl-BOPHYs as a sensitizer for triplet-triplet annihilation upconversion
Yuji Kubo

Abstract
Triplet-triplet annihilation upconversion (TTA-UC) has attracted increasing attention as promising method for energy conversion from low-energy excitation to higher energy light. In this study, the introduction of phenylselanide group at the 2- and 7- position of bis(difluoroboron)1,2-bis((1*H*-pyrrol-2-yl)methylene) hydrazine (BOPHY) core led to production of new triplet photosensitizer **1**. Setting up TTA-UC system of **1** and a triplet acceptor 9,10-diphenylanthracene allowed a UC emission with large anti-Stokes shift of 94 nm and UC quantum yield (Φ_{UC}) of 3.9% in toluene when excited with 524 nm laser (50 mW).

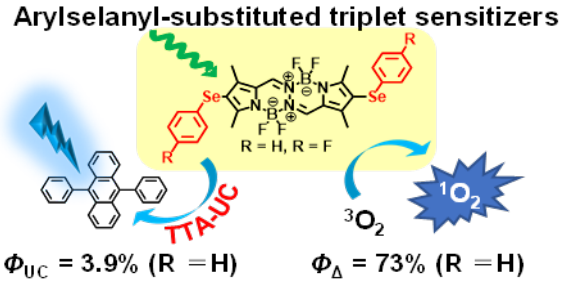


Figure 2. Arylselanyl-substituted BOPHYs as triplet sensitizers.

3. Synthesis of dye-sensitized photocatalysts for hydrogen Production
Yuji Kubo

Abstract
It is worthwhile to develop functional dyes that could contribute to the Sustainable Development Goals (SDGs). Given that photocatalysts for hydrogen production is remained to be researched due to its low efficiency. Sensitization of dye which has high light-harvesting capability is a promising approach for improving efficiency. In this study, benzofuran-fused BODIPY dye with cyanoacrylic acid as an anchoring group (**1**) was synthesized for the first time. Dye **1** has an intense absorption band at 605 nm ($\varepsilon = 1.07 \times 10^5\ M^{-1}\ cm^{-1}$) in THF. In the presentation, the photocatalytic activity of **1**-loaded TiO_2 is discussed.

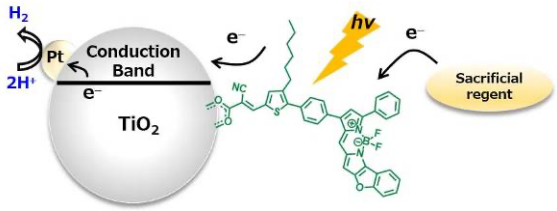


Figure 3. Dye-sensitized photocatalytic hydrogen production.

3. Visually chiral recognition using aggregation-induced emission
Yuji Kubo

Abstract
Detection of chirality is analytically significant because the enantio-purity of products is essential for various applications in the pharmaceutical, agrochemical, and food industry. Florescence sensing for chirality is a highly sensitive, facile, and cost-effective method for determining enantiomer purity. In this study, we focused on boronate ensembles with aggregation-induced emission (AIE) units because enantio-dependent aggregation modes provide the system with chiral sensors. However, the accuracy and repeatability of the change in the fluorescence signal as a function of the enantiomer excess of analytes are not high because self-assembly is used as an amplification method for molecular recognition events. We succeeded quantitative sensing chirality by applying chemometrics. Notably, calibration and prediction of the % ee of chiral **CHDA** was successfully achieved with the ANN technique.

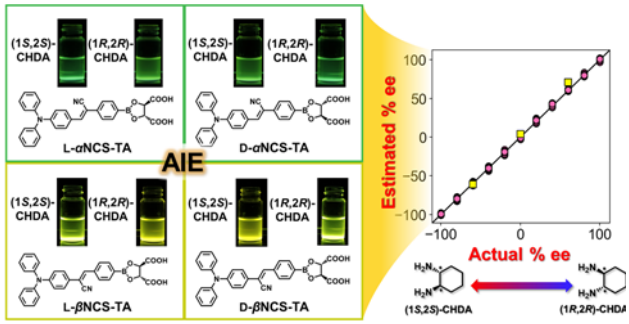


Figure 4. Chiral recognition coupled with chemometrics.

5. Sensor array based on cross reactivity using relay recognition

Yuji Kubo, Pavel Anzenbacher Jr

The prepared fluorescent carboxyamidoquinolines and their Zn(II) complexes were used to bind and sense various phosphate anions utilizing a relay mechanism, in which the Zn(II) ion migrates from the complex to the phosphate, namely adenosine 5'-triphosphate (ATP) and pyrophosphate (PPi), a process accompanied by a dramatic change in fluorescence. The cross-reactive nature of the carboxyamidoquinolines-Zn(II) sensors in conjunction with linear discriminant analysis (LDA) was utilized in a simple fluorescence chemosensor array that allows for the identification of ATP, ADP, PPi, and Pi from 8 other anions including adenosine 5'-monophosphate (AMP) with 100% correct classification. Furthermore, the support vector machine algorithm, a machine learning method, allowed for highly accurate quantitation of ATP in unknown samples with error < 2.5%.

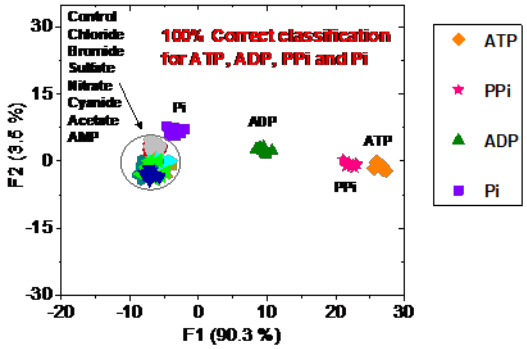


Figure 5. Graphical output of the qualitative linear discriminant analysis

6. Synthesis of boron-containing molecules for application in functional materials.

Masato Ito

Abstract

By the incorporation of main group elements into a π-conjugated skeleton, the main group element moieties can alter the π-skeleton sterically and electronically. Group 13 boron atom is of particularly interest, as its incorporation results in the low-lying LUMO through the p–π* interaction between a vacant p orbital of the boron atom and a π* orbital of a π-conjugated skeleton. Consequently, boron-containing π-conjugated skeletons exhibit the electron-accepting character together with high Lewis acidity. In this study, by taking advantage of these characteristics, we have achieved the development of a near-infrared luminescent dye with a narrow band width and a stimuli-responsive red emissive dye with the aim of constructing promising functional materials.

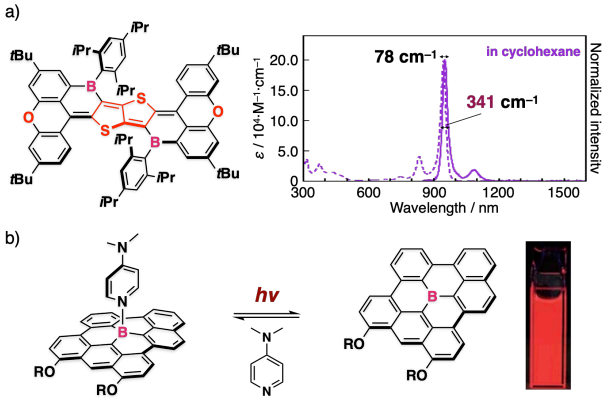


Figure 6. a) Moleculer structures of a near-infrared luminescent dye with a narrow band width and b) a stimuli-responsive red emissive dye.

■Papers with Peer Review

1. M. Kanakubo, Y. Yamamoto, and Y. Kubo, Room-temperature phosphorescence of thiophene boronate ester-cross linked polyvinyl alcohol; a triplet-to-singlet FRET-induced multi-color afterglow luminescence with Sulforhodamine B, *Bull. Chem. Soc. Jpn.*, **2021**, 94, 1204-1209. DOI:10.1246/bcsj.20210004

2. R. Hasegawa, S. Iwakiri, Y. Kubo, Synthesis and triplet sensitization of bis(arylselanyl)BOPHYs; potential application in triplet-triplet annihilation upconversion, *New J. Chem.*, **2021**, *45*, 6091-6099. DOI: 10.1039/D1NJ00721A

3. M. Ito, M. Sakai, N. Ando, S. Yamaguchi, Electron-deficient heteroacenes that contain two boron atoms: near-infrared fluorescence based on a push–pull effect, *Angew. Chem. Int. Ed.*, **2021**, *60*, 21853-21859. DOI: 10.1002/anie.202106642

4. M. Pushina, S. Farshbaf, W. Mochida, M. Kanakubo, Ryuhei Nishiyabu, Yuji Kubo, and P. Anzenbacher, Jr., A fluorescence sensor array based on zinc(II)-carboxyamidoquinolines: Toward quantitative detection of ATP, *Chem. Eur. J.*, **2021**, *27*, 11344-11351. DOI: 10.1002/chem.202100896

5. K. Makino, T. I, and Y. Kubo, A benzofuran[*b*]-fused BODIPY as an efficient sensitizer for photocatalytic hydrogen production, *Sustain. Energy Fuels*, **2021**, *5*, 3676-3686. DOI: 10.1039/D1SE00387A

6. K. Kawaguchi, A. Moro, S. Kojima and Y. Kubo, Chiral recognition coupled with chemometrics using boronate ensembles containing D-π-A cyanostilbenes, *Chem. Commun.*, **2021**,*57*, 12952-12955. DOI:10.1039/D1CC05492A.

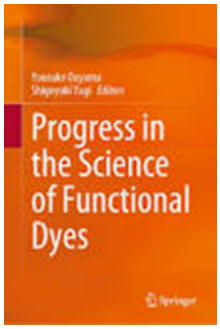
7. S. Farshbaf, K. Dey, W. Mochida, M. Kanakubo, R. Nishiyabu, Y. Kubo, and P. Anzenbacher Jr.,Detection of phosphates in water utilizing a Eu^{3+}- mediated relay mechanism, *New J. Chem.*, **2022**, 46, 1839-1844, DOI: 10.1039/d1nj04578d

8. H. Narita, H. Choi, M. Ito, N. Ando, S. Ogi, S. Yamaguchi, Fully fused boron-doped polycyclic aromatic hydrocarbons: their synthesis, structure–property relationships, and self-assembly behavior in aqueous media, H. Narita, H. Choi, M. Ito,

N. Ando, S. Ogi, S. Yamaguchi, *Chem. Sci.*, **2022**, *13*, 1484–1491. DOI: 10.1039/D1SC06710A

■Books

1. White-Light Emissive Materials Based on Supramolecular Approach, Yuji Kubo, Progress in the Science of Functional Dyes, Editors ; Yousuke Ooyama 、Shigeyuki Yagi, 2021, Springer, Pages 409-443.



■Invited Lectures

See the annual report in Japanese (1) article.

■Academic Meeting

＊International

1. Electron push–pull effect on the properties of two boron-containing electron-deficient heteroacenes, Masato Ito, Mika Sakai, Naoki Ando, Shigehiro Yamaguchi, Beyond Telluride Forum (online), Apr. 13, 2021.
2. Accurate pattern recognition for chiral amines from just a single chemosensor, Yui Sasaki, Soya Kojima, Vahid Hamedpour, Riku Kubota, Shin-ya Takizawa, Isao Yoshikawa, Hirohiko Houjou, Yuji Kubo, Tsuyoshi Minami, Pacifichem 2021, Optical Cross-Reactive Sensor Arrays, Artificial Noses and Tongues (#352), Dec.18, 2021.
3. Boron-stabilized radicals: fluorescence properties and application to organic light-emitting diodes, Masato Ito, Yongfa Xie, Naoki Ando, Tomokatsu Kushida, Shunsuke Shirai, Hiroki Soutome, Kenichi Tabata, Yasuo Miyata, Hiroshi Kita, Shigehiro Yamaguchi, Pacifichem 2021, Designed pi-Electronic Systems: Synthesis, Properties, Theory and Function (#359), Dec. 19, 2021.
4. Boron-doped polycyclic aromatic hydrocarbons with unsymmetric structures, Hiroki Narita, Masato Ito, Naoki Ando, Soichiro Ogi, Shigehiro Yamaguchi, Pacifichem 2021, Designed pi-Electronic Systems: Synthesis, Properties, Theory and Function (#359), Dec. 19, 2021.

＊Domestic

See the annual report in Japanese (15) articles.

■Awards

See the annual report in Japanese.

Setaka Laboratory

■**Members**
Wataru Setaka
Professor /Dr. Sci.
Physical Organic Chemistry, Functional Organic Chemistry
room: 9-542 TEL: +81-42-677-1111 (Ext.4955)
e-mail: wsetaka@tmu.ac.jp

Yusuke Inagaki
Assistant Professor / Dr. Sci.
Main-group Chemistry, Functional Organic Chemistry
room: 9-545 TEL: +81-42-677-1111 (Ext.4957)
e-mail: yinagaki@tmu.ac.jp

Doctor's course -0
Master's course -7
Bachelor 9

■**Outlines of the Research**

Development of Highly Designed Organic Molecules

Development of organic molecules of which strucrure and functions are highly designed would improve our daily life with respect to energy saving and environmental consequence. Our interest lies in the design and synthesis of organic molecules with new structures that incorporate silicon to develop molecules with new functions. Specifically, we are studying the relationship between molecular structure and molecular functionalities of novel organosilicon compounds.

1. Crystalline Molecular Gyrotop

A molecular machine has been defined as a discrete number of molecular components that perform mechanical-like movements in response to specific stimuli. Macrocage molecules with a bridged rotor have been synthesized as molecular gyroscopes and molecular gyrotops given that the rotor can rotate even in the crystalline state.

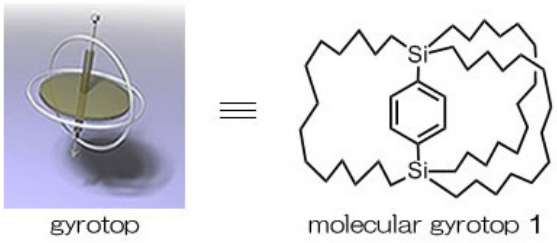


Figure 1. molecular gyrotop.

In this year, following papers were published.
Fluorescent dielectric materials that show solid-state fluorescence and dielectric relaxation in the crystalline state were realized using crystals of thienothiophene-dioxide-bridged macrocage compounds C14TTO2 and C18TTO2, in which the first number indicates the length of the alkyl chains in the cage. In these molecules, the fluorophore can rotate even in the crystalline state because the fluorophore is encased in the macrocage frame. Therefore, they are called molecular gyrotops. The rotational dynamics of the fluorophore in the crystalline state were observed by temperature-dependent dielectric relaxation, and the fluorophore was found to be static in C14TTO2, while restricted rotation was observed for C18TTO2. The solid-state fluorescence quantum yield decreased with the increasing alkyl chain length, indicating that the fluorescence intensity clearly depends on the dynamics of the fluorophore. (Figure 2, paper #3).

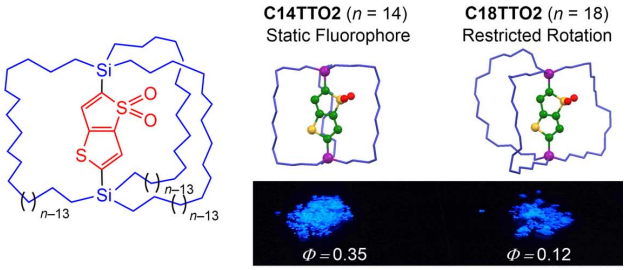


Figure 2. Structural formulas, X-ray structures of thienothiophene dioxide bridged molecular gyrotops, and photographs of fluorescence of their powder samples (paper #3).

Intramolecular charge transfer (ICT) fluorescence has been widely investigated and exploited in sensor molecules. However, steric effects on the ICT fluorescence properties have rarely been reported so far, although research in this area would promote an understanding of the basics of solvation. Herein, we report the detailed fluorescence properties of bis(trimethylsilyl)benzo[b]thiophene-1,1-dioxide (TMSBTO2) and its caged cyclophanes and non-cage isomers, which demonstrate ICT fluorescence in various solutions. The fluorescence band maxima for these benzo[b]thiophene-1,1-dioxides (BTO2s) showed a red-shift with increasing solvent polarity, confirming ICT fluorescence characteristics. The linearity of the Lippert–Mataga plots was confirmed for all ICT fluorescence measured in hexane, toluene, AcOEt, CH2Cl2, and EtOH. The slopes of the plots decreased in the following order: TMSBTO2, non-cage isomers, and caged BTO2s. It is concluded that the Onsager radii for these BTO2s were increased in the abovementioned order, assuming that the difference in the dipole moments between the excited and ground states for these BTO2s was identical. (Figure 3, paper #2).

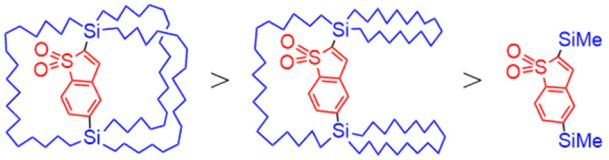


Figure 3. Order of Onsagar radii for ICT fluorescence in silyl substituted benzothiophene dioxides (paper #2).

2. Novel Flexible Macrocycles

A facile and novel template synthesis of flexible disilamacrocyclic compounds via a ring-closing metathesis coupling was achieved. The structures of the macrocycles were determined by X-ray crystallography, and two conformers with similar stabilization energies were observed and characterized. (Figure 5, paper #4).

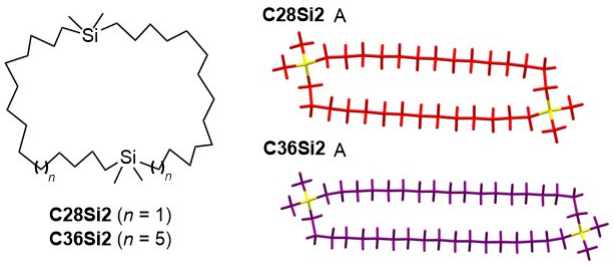


Figure 5. Structure of disilamacrocycles in a crystalline state (paper #4).

Facile and simultaneous synthesis of diphenyl-disilabicyclo[14.14.14]alkane in/out-isomers was achieved by using organosilicon chemistry. Although the formation of several in/out-isomers would be conceivable, only two diastereomers, i.e. the (traditional-)out,out-isomer and the twist-out,out-isomer, could be isolated because of homeomorphic isomerization. Crystal structures of the diastereomers were confirmed (Figure 6, paper #1).

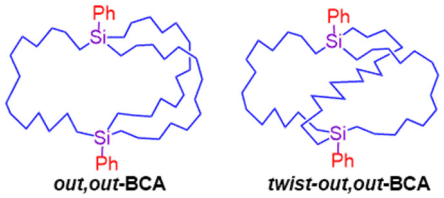


Figure 6. Structural formulas of disilabicycloalkanes (paper #1).

■Papers with Peer Review

1. Simultaneous Synthesis and Characterization of in/out-Isomers of Disilabicyclo[14.14.14]alkanes, Yuto Ikeda, Yusuke Inagaki, and Wataru Setaka*, *Chem. Commun.* **2021**, *57*, 7838-7841.
2. Steric effects on the intramolecular charge transfer fluorescence of benzo[b]thiophene-1,1-dioxide bridged macrocages, Keita Nobuhara, Yusuke Inagaki, and Wataru Setaka*, *Org. Biomol. Chem.* **2021**, *19*, 6328-6333.
3. Crystalline Thieno[3,2-b]thiophene-dioxide-diyl bridged Molecular Gyrotops as Fluorescent Dielectric Materials, Daiki Hayashi, Yusuke Inagaki, and Wataru Setaka*, *J. Mater. Chem. C* **2021**, *9*, 8220-2225.
4. Structure and Dynamics of Crystalline Molecular Gyrotops with a Difluorophenylene Rotor, Yuyang Tu, Yusuke Inagaki, Eunsang Kwon, and Wataru Setaka*, *Chem. Lett.* **2021**, *50*(7), 1397-1399.
5. Structure and Dynamics of Crystalline Molecular Gyrotops with a Difluorophenylene Rotor, Taro Tsuchiya, Yusuke Inagaki, Kentaro Yamaguchi, and Wataru Setaka*, *J. Org. Chem.* **2021**, *86*(3), 2423–2430.
   DOI: 10.1021/acs.joc.0c02571N
6. Solid-State ^{2}H NMR Study for Deuterated Phenylene Dynamics in a Crystalline Gyroscope-Like Molecule, Wataru Setaka*, Kentaro Yamaguchi, Mitsuo Kira, *Chemistry* **2021**, *3*(1), 49, 39–44. (A Special Issue in Honor of Professor J. Michl)

■Invited Lectures

1. Yusuke Inagaki,
   Substituent Effect as a New Phospher in Silylfuryl Substituted Fluorobenzene
   The 25st Symposium on Silicon Chemistry, Online, 2021.10.28 (Japan).(oral, in Japanese)

2. Wataru Setaka,
   Chemistry of Molecular Gyrotops as Molecular Machines
   Special Lec. for Graduate School Students (1), Tokyo University of Science, 2021.7.7. (oral, in Japanese)

■Academic Meeting

＊Domestic

See the annual report in Japanese (13 articles)

Kanamura Laboratory

■**Members**
Kiyoshi KANAMURA
Professor /Dr. Eng.
Inorganic Industrial Chemistry, Energy Chemistry, Electrochemistry
room:9-247 TEL: +81-42-677-2828
e-mail: kanamura@tmu.ac.jp

Hirokazu MUNAKATA
Assistant Professor /Ph.D.
Electrochemistry, Inorganic Material Chemistry, Batteries and Fuel Cells
room:9-246 TEL: +81-42-677-2826
e-mail: munakata@tmu.ac.jp

Doctor's course - 1
Master's course - 13
Bachelor 4 - 0

■**Outlines of the Research**

1. Research on next-generation rechargeable batteries
Kiyoshi KANAMURA, Hirokazu MUNAKATA

The development of rechargeable lithium batteries with lithium-metal anode was carried out to realize higher energy density than that of currently-used lithium-ion batteries. Lithium-metal anode has about ten times larger gravimetric capacity than graphite anode used in lithium-ion batteries. However, its morphology changes to needle-like forms during charge-discharge cycles, resulting in internal short circuit of batteries by the penetration of a separator. Low Coulombic efficiency due to easy decomposition of electrolyte solutions on lithium metal is also a problem to be solved. In this year, the optimization of electrolyte composition and separator structure were mainly carried out to solve those problems. In addition, laminate type cells were constructed and tested instead of coin type ones to extract issues on practical cell design.

From the pressure visualization measurement, laminate type cells showed more uniform pressure distribution than coin type cells, improving the uniformity of lithium deposition morphology. The laminate type cells with $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ (NCM523) composite cathode and 20 μm lithium metal anode were fabricated using 1 mol dm^{-3} $LiPF_6$ / ethylene carbonate (EC) electrolyte solution including different amounts of fluoroethylene carbonate (FEC) as an electrolyte additive (Fig. 1). The cell without FEC showed a decrease in the capacity retention after about 30th charge-dsicahrge cycle. On the other hand, the improved capacity retention was observed for all the cells including FEC, and the highest cycleability was obtained in that with 3 wt.% FEC (Fig. 2).

Fig. 1 A laminate type rechargeable lithium-metal battery prepared in this study.

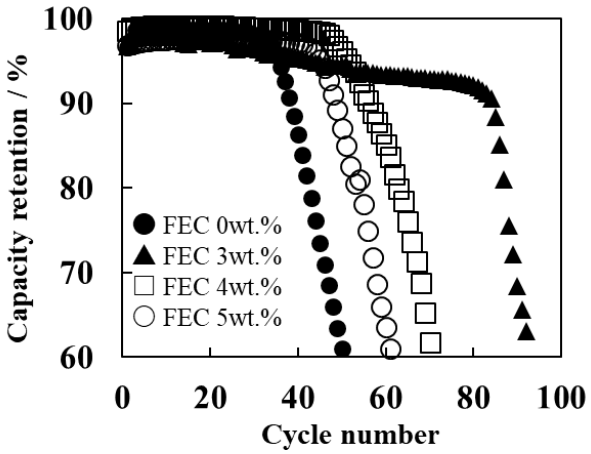


Fig. 2 Capacity retention of laminate type rechargeable lithium metal batteries composed of NCM523 composite cathode and 20 μm lithium metal anode including different amounts of FEC in 1 mol dm^{-3} $LiPF_6$ / EC electrolyte solution.

2. Research on fuel cells
Kiyoshi KANAMURA, Hirokazu MUNAKATA

To improve the energy conversion efficiency of fuel cells, the operation at higher temperatures is basically needed, which enables to use waste heat more effectively in addition to the activity improvement and poisoning suppression of fuel cell catalysts. We have focused on H^+-conducting ionic liquids and their mixtures with phosphoric acid as new electrolytes usable at around 200 °C, and been developing the intermediate temperature fuel cells.

To achieve better fuel cell performance, we focused and tried to improve the electrochemical oxygen reduction reaction (ORR) of catalysts in the ionic liquid-based electrolytes continuously in this year. By using nitrogen-doped graphene as Pt catalyst support instead of conventionally used Ketjen black, we succeeded to improve ORR activity and durability of Pt catalyst in those electrolytes (Fig. 3). In addition, we focused on the application of OH^--conducting ionic liquids as new electrolytes for intermediate temperature operation of alkaline-type fuel cells, and revealed that carbon-based materials have higher ORR activity than Pt catalyst in those OH^--conducting ionic liquids.

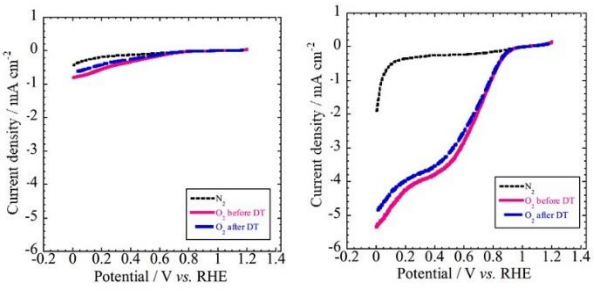


Fig. 3 ORR activity and durability of Pt/C (left) and Pt/nitrogen-doped graphene (right) in H^+-conducting ionic liquid composed of N,N-diethylmethylamine and trifluoromethanesulfonic acid (black lines: N_2 atmosphere before durability test, red lines: O_2 atmosphere before durability test, blue lines: O_2 atmosphere after durability test) at 120 °C. The durability test was performed by 2000 cycles of potential sweep at 500 mV s^{-1} in a potential range of 1.0~1.5 V vs. RHE.

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1. Mayu Saito, Hidechika Arima, Mao Shoji, Yota Kizuki, Hirokazu Munakata, Kiyoshi Kanamura, Koichi Kajihara, Solid-State Rechargeable Lithium Metal Battery with $Li_4B_4Al_3O_{12}Cl$-based Water-Resistant Lithium-Ion-Conducting Oxychloride Glass-Ceramic Electrolyte, Journal of The Electrochemical Society, 168 (2021) 040524.
2. Dong Ding, Yuta Maeyoshi, Masaaki Kubota, Jungo Wakasugi, Koshin Takemoto, Kiyoshi Kanamura, Hidetoshi Abe, Li-ion conducting glass ceramic (LICGC)/reduced graphene oxide sandwich-like structure composite for high-performance lithium-ion batteries, Journal of Power Sources, 500 (2021) 229976.
3. Dong Ding, Yuta Maeyoshi, Masaaki Kubota, Jungo Wakasugi, Kiyoshi Kanamura, Hidetoshi Abe, Non-flammable super-concentrated polymer electrolyte with “solvated ionic liquid” for lithium-ion batteries, Journal of Power Sources, 506 (2021) 230099.
4. Koichi Kajihara, Daisuke Takahashi, Hiroaki Kobayashi, Toshihiko Mandai, Hiroaki Imai, Kiyoshi Kanamura, Phenylphosphonate surface functionalisation of $MgMn_2O_4$ with 3D open-channel nanostructures for composite slurry-coated cathodes of rechargeable magnesium batteries operated at room temperature, RSC Advances, 11 (2021) 19076-19082.
5. Jik Soo Kim, Seonghyeon Lim, Hirokazu Munakata, Sung-Soo Kim, Kiyoshi Kanamura, Understanding the relationship of electrochemical properties and structure of microstructure-controlled core shell gradient type Ni-rich cathode material by single particle measurement, Electrochimica Acta, 390 (2021) 138813-138818.
6. Toshiki Tsuchiya, Yuko Fukuda, Kiyoshi Kanamura, Koichi Kajihara, Low-Refractive-Index Deep-Ultraviolet Transparent Poly(fluoroalkyl-co-methylsilsesquioxane) Resins Synthesized by Cosolvent-Free Hydrolytic Polycondensation of Organotrimethoxysilanes, Journal of Physical Chemistry B, 125 (2021) 8238-8242.
7. Eric Jianfeng Cheng, Mengyue Liu, Ying Li, Takeshi Abe, Kiyoshi Kanamura, Effects of porosity and ionic liquid impregnation on ionic conductivity of garnet-based flexible sheet electrolytes, Journal of Power Sources, 517 (2022) 230705.
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9. Hossein Davoodi, Nurdiana Nordin, Hirokazu Munakata, Jan G. Korvink, Neil MacKinnon, Vlad Badilita, Untuned broadband spiral micro-coils achieve sensitive multi-nuclear NMR TX/RX from microfluidic samples, Scientific reports, 11 (2021) article number 7798.

■Books and reviews

See the annual report in Japanese (4 articles)

■Invited Lectures

＊Domestic

See the annual report in Japanese (1 article)

■Requested Lectures

＊Domestic

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■Academic Meeting

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Kajihara Laboratory

■**Members**
Koichi KAJIHARA
Professor /Ph.D.
Inorganic Chemistry, Functional Material Chemistry,
Inorganic Materials/Physical Properties
Room:9-336 TEL: +81-42-677-2827
kkaji@tmu.ac.jp

Takashi TAKEI
Associate Professor/Dr. Eng.
Solid Surface Chemistry, Colloid and Interface Science
Room. 9-142 TEL:+81-42-677-2822
takei-takashi@tmu.ac.jp

Takashi YANAGISHITA
Associate Professor/ Dr. Eng.
Electrochemistry, Functional Metal Oxide Film
Room. 9-140 TEL:+81-42-6 77- 1111 (Ext. 4931)
yanagish@tmu.ac.jp

Master's course -11
Bachelor 4 -9

■**Outlines of the Research**

1. Studies on inorganic materials and energy devices
Koichi KAJIHARA

We are studying energy devices using oxides. A new lithium chloroboracite $Li_4B_4Al_3O_{12}Cl$ discovered in our lab. is stable in contact with lithium. It was found to be water-resistant and usable as solid electrolytes of solid rechargeable lithium metal batteries (Fig. 1). We have also developed phenylphosphonate surface functionalization of porous $MgMn_2O_4$, a promising cathode material for rechargeable magnesium batteries, and found that this method is effective in suppressing side reactions during charge and discharge, increasing Coulombic efficiency, improving the quality of slurry-coated cathodes, and achiving the room temperature operation of slurry-coated cathodes with high active material contents (Fig. 2).

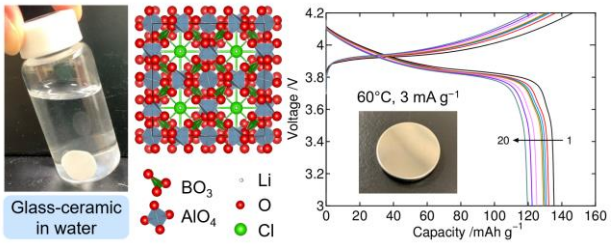

Fig. 1 A coin-type solid-state rechargeable lithium metal battery prepared using water-resistant glass-ceramic electrolyte of a new lithium boracite $Li_4B_4Al_3O_{12}Cl$.

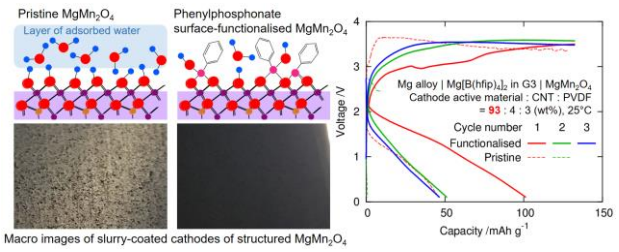

Fig. 2 Phenylphosphonate surface functionalization of porous $MgMn_2O_4$ for rechargeable magnesium batteries and operation of slurry-coated cathodes with high active material contents at room temperature.

Silica is a ubiquitous material and its utilization is in accordance with SDGs. We are studying cosolvent-free sol-gel method to form silca-based materials only from silicon alkoxides and water without using cosolvents. Using this method we prepared fluorine-containing low-refractive-index and deep-ultraviolet-transparent resins and achived a refractive index of ~1.35 at 589 nm (Fig. 3) We also found that silica-(Tb,Ce)PO_4 transparent glass-ceramics prepared by a cosolvent-free sol-gel mehod exhibit consentration-quenching-free green photoluminescene with internal quantum efficiency close to unity, whereas that of (Tb,Ce)–Al-codoped silica glasses, in which rare-earth ions are rather disersed, is much lower. These observations demonstrate that the control of the distribution of rare-earth ions is crucial in increasing the photoluminescence quatum efficiency of rare-earth-doped silica glasses (Fig. 4).

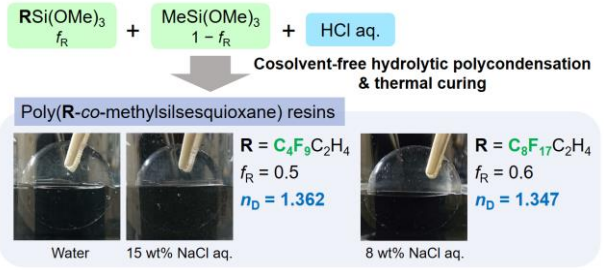

Fig. 3 Fluorine-containing low-refractive-index polysilsesquioxane resins prepared by a cosolvent-free method.

Fig. 4 Concentration-quenching-free green photoluminescence of a silica–(Tb,Ce)PO_4 transparent glass-ceramic (left) and green photoluminescence of a (Tb,Ce)–Al-codoped silica glass under excitation with an UV LED at 290 nm.

2. Verification of pore size distribution measurement methods using porous solid by packed spheres
Takashi TAKEI

Pore size distribution is used for evaluating the basic physical properties of porous materials. The realistic pore model has been prepared by the packed silica spheres. The pore size distribution has been evaluated from the nitrogen adsorption method, thermoporometry, and mercury-intrusion-porosimetry. Comparative study of three methods have revealed the character of these methods and the validity of the application to porous solids having various pore shapes.

3. Fabrication of Nanofilters by Electrochemical Process
Takashi YANAGISHITA

For the fabrication of ordered nanofilere membranes, we have investigated anodization process of Al. The size and interval of holes could be controlled by adjusting the anodization conditions. Metal and semiconductor nanohole array structures have been also fabricated using an anodic porous alumina as a template. For the replacement of the ordered hole-array structure with other materials we developed a two-step replication process in which formation of a replicated negative and subsequent preparation of a replicated positive give the nanohole structure identical to that of mother structure of anodic orous alumina. Metal (Au, Pt, Ni) and semiconductor (TiO2, ZnO, CdS) nanohole arrays have been fabricated using the two-step process. Detailed conditions for the precise replication were examined experimentally, and new applications, such as optical devices and detector for low energy ions, have been developed

4. Preparation of Ordered Nanostructures by Nanoimprinting Using Ordered Anodic Porous Alumina Molds

Takashi YANAGISHITA

Ordered pillar array and hole array patterns were fabricated by nanoimprinting using anodic porous alumina. Patterned surface prepared by this process could be used for the antirefrection surface and surper hydrophobic surface.

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1. K. Kajihara, S. Nakagawa, R. Iwasaki, Energy transfer and quenching in sol–gel-derived silica glass green phosphors doped with Tb^{3+} and Ce^{3+} ions: Distinct difference between P- and Al-codoped glasses. Phys. Status Solidi A 219, 2100494 (2022)
2. T. Tsuchiya, Y. Fukuda, K. Kanamura, K. Kajihara. Low-refractive-index deep-ultraviolet transparent poly(fluoroalkyl-co-methyl-silsesquioxane) resins synthesized by cosolvent-free hydrolytic polycondensation of organotrimethoxysilanes. J. Phys. Chem. B 125, 8238-8242 (2021).
3. K. Kajihara, D. Takahashi, H. Kobayashi, T. Mandai, H. Imai, K. Kanamura. Phenylphosphonate surface functionalisation of $MgMn_2O_4$ with 3D open-channel nanostructures for composite slurry-coated cathodes of rechargeable magnesium batteries operated at room temperature. RSC Adv. 11, 19076-19082 (2021). Open Access
4. L. Skuja, N. Ollier, K. Kajihara, I. Bite, M. Leimane, K. Smits, A. Silins. Optical absorption of excimer laser-induced dichlorine monoxide in silica glass and excitation of singlet oxygen luminescence by energy transfer from chlorine molecules. Phys. Status Solidi A 218, 2100009 (2021).
5. M. Saito, H. Arima, M. Shoji, Y. Kizuki, H. Munakata, K. Kanamura, K. Kajihara. Solid-state rechargeable lithium metal battery with $Li_4B_4Al_3O_{12}Cl$-based water-resistant lithium-ion-conducting oxychloride glass-ceramic electrolyte. J. Electrochem. Soc. 168, 040524 (2021).
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9. T. Yanagishita, H. Itoh, and H. Masuda. Efficient Fabrication of Ordered Alumina Through-Hole Membranes Using TiO2 Protective Layer Prepared by Atomic Layer Deposition. RSC Adv., 12, 3662 (2022).
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12. T. Yanagishita, K. Kikkawa, and H. Masuda. Ideally ordered anodic porous alumina on Si substrate prepared by anodization of sputtered Al-Mg thin film. ECS J. Solid State Sci. Technol., 10, 115002 (2021).
13. T. Yanagishita, Y. Nishioka, S. Miwa, H. Masuda, Y. Komoda. Template-Free Preparation of Metal Nanowires by Two-Phase Electrolysis Using Cells Composed of Water and Oil Phases. J. Electrochem. Soc., 168, 093502 (2021).
14. T. Yanagishita, M. Yoshida, H. Masuda. Renewable Superhydrophobic Surfaces Prepared by Nanoimprinting Using Anodic Porous Alumina Molds. Langmuir, 37, 10573 (2021).
15. T. Yanagishita, M. Otsuka, T. Takei, U. Seigo, H. Masuda. Preparation of Ordered Anodic Porous Alumina with Single-Nanometer-Order-Size Holes by Atomic Layer Deposition. Langmuir, 37, 8331 (2021).
16. T. Kondo, M. Yoshida, T. Yanagishita, H. Masuda. Fabrication of Li Nanohole Array by Replication Process Using Anodic Porous Alumina Template. J. Electrochem. Soc., 168, 032508 (2021).

■Reviews and Books

See the annual report in Japanese (2 articles)

■Invited Lectures

＊Internationa

1. K. Kajihara, Acid-catalyzed tetraalkoxysilane-water binary solutions: liquid-state NMR characterization and silica thin film processing. PACRIM14, 2021/12, online.

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See the annual report in Japanese (4 articles)

■Academic Meeting

＊International

1. K. Kajihara, R. Iwasaki, Negligible concentration quenching in sol–gel-derived silica–$(Tb,Ce)PO_4$ transparent glass-ceramic green phosphors. SiO_2 2021(Lille France), 2021/6, online.
2. M. Martínez-Viademonte, S. T. Abrahami, T. Yanagishita, K. Thiel, M. D. Havigh, B. Wouters, T. Hack, M. Burchardt, H. Terryn. Modification of porous anodic layers on AA2024 clad by atomic layer deposition and its effect on coating adhesion and oxide stability. EUROCORR 2021, 2021/6, online

＊Domestic

See the annual report in Japanese (28 articles)

■Patents

See the annual report in Japanese (1 articles)

■Awards

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Takagi Laboratory

■**Members**
Shinsuke TAKAGI
Professor /Ph.D
Photochemistry, Photo-functional Materials Chemistry, Porphyrin Chemistry, Clay Science
Room: 9－446 TEL: +81-42-677-2839
e-mail: takagi-shinsuke@tmu.ac.jp

Tamao ISHIDA
Associate Professor /Dr. Eng.
Catalysis Chemistry
room:9-B51 TEL: +81-42-677-2845
e-mail: tamao@tmu.ac.jp

Tetsuya SHIMADA
Assistant Prof. / Ph.D.
Physical Chemistry, Spectroscopy
Room: 9-445 TEL: +81-42-677-1111 (Ext.4897)
e-mail: shimada-tetsuya@tmu.ac.jp

Visiting researcher 4
Doctor's course 7
Master's course 13
Bachelor 8
Research student 1

■**Outlines of the Research**

Our group challenges to control photochemical reactions such as electron and energy transfer, by controlling the orientation and alignment of dyes on the inorganic surfaces. Recently, organic/inorganic hybrids composed of porphyrins and layered materials have been the subject of intensive investigations to explore their novel properties and functionalities. We found out that a precise matching of distances between the negatively charged sites on the clay mineral layers and that between the positively charged sites in the dye molecule is one of the most important factors to determine the structure of the clay–dye complex. We have termed this the "Size-Matching Rule". Our goal is finding out a new methodology to control molecular assembly structure and realizing functionalized photochemical reaction systems such as an artificial light harvesting system.

1. Research on Artificial Light Harvesting System
Shinsuke TAKAGI, Tetsuya SHIMADA

The quantitative excited energy transfer reaction between cationic porphyrins on an anionic clay surface was successfully achieved. The efficiency reached up to ca. 100% owing to the "Size- Matching Rule" that is our original technique. It was revealed that the important factors for the efficient energy transfer reaction are (i) suppression of the self-quenching between adjacent dyes, and (ii) suppression of the segregated adsorption structure of two kinds of dyes on the clay surface. These findings indicate that the clay/porphyrin complexes are promising and prospective candidates to be used for construction of an efficient artificial light-harvesting system. Especially when phthalocyanine was used as energy acceptor, light harvesting type energy transfer was realized. In addition to these, hydrogen evlution systems using sunlight as an energy source has been developed. Especially, photochemical hydrogen and hydroperoxide formation were examined as an energy related subject this year.

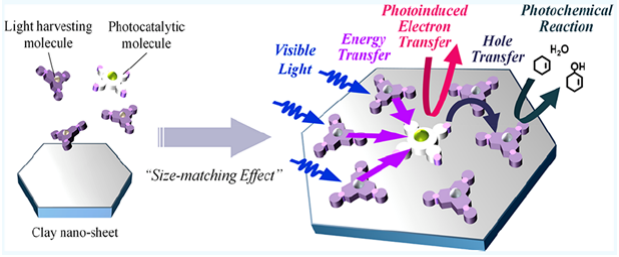


Fig. 1. Artificial light harvesting model on the nanosheet.

2. Research on Novel Methodology to Control the Adsorption Structure of Dyes on the Clay Surface
Shinsuke TAKAGI, Tetsuya SHIMADA

Saponite-type clays that have different cation exchange capacities were successfully synthesized by hydrothermal synthesis. The structure and properties were analyzed by X-ray diffraction, X-ray fluorescence, ^{27}Al NMR, FT-IR, thermogravimetric and differential thermal analysis, atomic force microscopy, and cation exchange capacity measurement. The intercharge distances on the synthetic saponite (SS) surfaces were calculated to be 0.8-1.9 nm on the basis of a hexagonal array. The complex formation behavior between SS and cationic porphyrins was examined. It turns out that the average intermolecular distance between porphyrin molecules on the SS surface can be controlled, depending on the charge density of the SS. The adsorption behavior of porphyrin on the SS surface can be rationally understood by the previously reported "size-matching rule". This methodology using host-guest interaction can realize a unique adsorption structure control of the porphyrin molecule on the SS surface, where the gap distance between guest porphyrin molecules is rather large. These findings will be highly valuable to construct photochemical reaction systems such as energy transfer in the complexes. In this year, the glass substrate was examined as a novel host material to control the nano-structure of dye assembly.

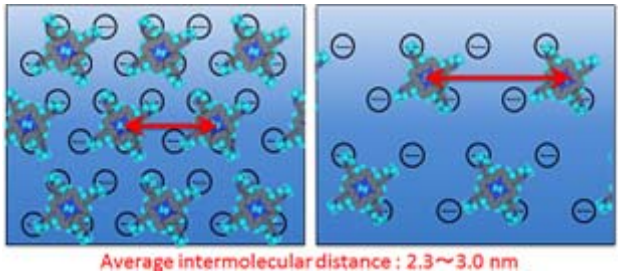


Fig. 2. An example of our methodology to control the adsorption structure of dyes on the clay surface by using a suitable clay species.

3. Unique Enzyme Activity of Peroxidase on a Clay Nanosheet
Shinsuke TAKAGI, Tetsuya SHIMADA

The adsorption behavior and enzyme activity of horseradish peroxidase (HRP) was examined on a synthetic clay nanosheet, whose surface is flat at the atomic level and is negatively charged. The results showed that HRP is adsorbed effectively (adsorption equilibrium constant, $K = 1.61 \times 10^7$ L mol^{-1}) and that the structure of HRP was altered on the clay surface. The enzyme activity of HRP on the clay surface was evaluated by using H_2O_2 and tert-BuOOH as a substrate. As a result, HRP on the clay surface was able to work for tert-BuOOH, while HRP in solution did not show any activity. In addition, HRP on SSA showed reactivity even under the high-temperature conditions. These results indicate that the clay nanosheet can be a unique modifier for enzyme activity of HRP.

4. Surface – Fixation Induced Emission on the nanosheets

Shinsuke TAKAGI, Tetsuya SHIMADA

We investigated the fluorescence enhancement behavior of AIE (Aggregation Induced Emission) – active dyes on the clay nanosheet. Judging from their adsorption observation on the clay in water, the factor for the fluorescence enhancement is turned out not to be AIE, but is to be Surface - Fixation Induced Emission (S - FIE) mechanism. While the effect of AIE depended on the molecular structure of dye in water-dioxane, S - FIE worked even for the dye that has bulky substituent. In this year, not only fluorescence but also phosphorescence was examined as a photochemical behavior. As a result, the enhancement of phosphorescence on clay surface was found put.

Fig. 3. Surface – Induced Emission on the nanosheets. Left: without nanosheet, Right: with nanosheet.

5. Research on Dye Sensitized Hydrogen Evolution System using titania nanosheet

Shinsuke TAKAGI, Tetsuya SHIMADA

Visible light induced hydrogen evolution system was constructed by using Rh doped titania nanosheet (Rh-TNS) as an adsorbent, an electron accepter, and a photocatalyst for H_2 production with 5.0% quantum yield. The action spectra for hydrogen production were well coincide with the absorption spectra of Zn-porphyrin that was adsorbed on Rh-TNS.

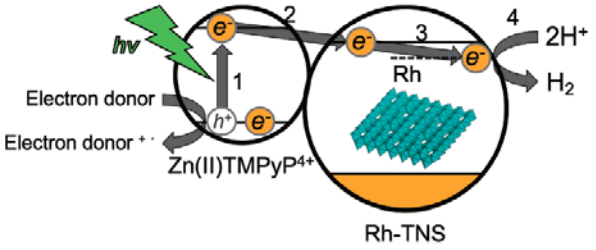


Fig. 4. Electron injection from Dye to semiconductor nanosheet.

6. "In-water" Dehydration Reaction of an Aromatic Diol on an Inorganic Surface

Shinsuke TAKAGI, Tetsuya SHIMADA

The effect of a synthetic saponite surface on the "inwater" dehydration reaction of diol was examined using 4-formyl-1-methylquinolinium salt (MQu^+) as a substrate. The equilibrium between aldehyde (MQu^+-Aldehyde) and diol (MQu^+-Diol) was affected by the surrounding environment. The equilibrium behavior was observed by ^1H nuclear magnetic resonance (NMR) and UV−vis absorption measurements. Although MQu^+ was completely in the form of MQu^+-Diol in water, the equilibrium almost shifted to the MQu^+-Aldehyde side when MQu^+ was adsorbed on the saponite surface in water. In addition, the MQu^+- Aldehyde ratio depended on the negative charge density of saponite. The factors that determine MQu^+-Aldehyde: MQu^+-Diol ratio were discussed from the thermodynamic analysis of the system. These data indicate that the electrostatic interaction between the charged saponite surface and MQu^+ stabilized the aldehyde side enthalpically and destabilized it entropically. The major reason for these results is considered to be the difference in adsorption stabilization between MQu^+-Aldehyde and MQu^+-Diol on saponite surfaces.

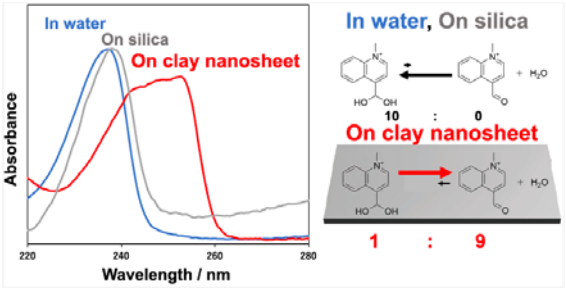


Fig. 5. The equilibrium between aldehyde (MQu^+-Aldehyde) and diol (MQu^+-Diol) in water without and with clay nanosheet.

7. Research on supported gold catalysts

Tamao ISHIDA

Hydroxyapatite (HAP)-supported gold nanoparticle (Au NP) catalysts exhibit a strong metal-support interaction (SMSI), in which a thin layer of HAP covers the surface of Au NPs by heat treatment under oxidative atmosphere. In addition, the electronic properties of Au tend to be cationic by the expression of SMSI. We investigated whether this oxidative SMSI occurs in cation- and anion-substituted HAPs (sHAPs), and how the electronic state of Au NPs changes. Utilizing the SMSI-induced cationic properties of Au, the isomerization of 3,4-diacetoxybut-1-ene (34DABE) to 1,4-diacetoxybut-2-ene (14DABE) was examined.

For all the Au/sHAP catalysts treated at 300 °C under O_2 (Au/sHAP_300_O_2), the surface of Au particles was partially covered by thin sHAP layers, confirmed by high-resolution transmission electron microscopy (HRTEM) (Fig. 6). Au NPs with a mean diameter of ca. 2 nm were deposited on unsubstited HAP (CaHAP, $Ca_{10}(PO_4)_6(OH)_2$) regardless of whether the thermal treatment atmosphere was O_2 or H_2, i.e., the presence or absence of SMSI. On the other hand, when the hydroxy group of CaHAP was replaced by a floride ion (CaFAP) and reduced in H_2, large Au NPs with a mean diameter of 9 nm were deposited, while the mean diameter of Au decreased to ca. 2 nm under O_2. It suggests that the aggregation of Au was suppressed by the formation of SMSI. When the phosphate in HAP was replaced by vanadate (VO_4) (SrVAP), relatively large Au NPs (ca. 5 nm) were deposited. These results suggest that phosphate and hydroxide groups play an important role for stabilizing Au particles. When Ca was replaced by Sr (SrHAP), obviouos difference in the Au particle size was not observed compared to CaHAP, but a partial substitution of Ca with Mg or Ce was effective for minimizing the Au particle size, giving Au clusters with diameters of less than 2 nm. For all the Au/sHAPs, the sizes of Au NPs were almost the same between O_2- and H_2-treated samples except for Au/CaFAP.

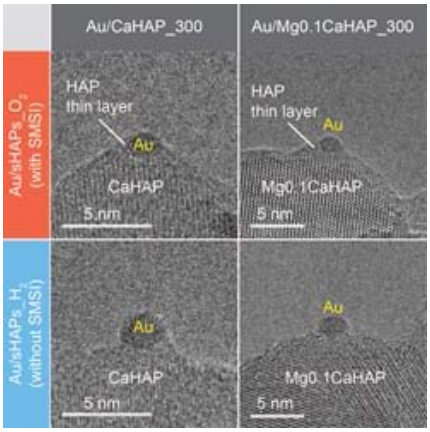


Fig. 6 HRTEM images of Au/CaHAP and Au/Mg0.1CaHAP heat-treated at 300 °C under O_2 (with SMSI) and H_2 (without SMSI).

The electronic states of Au of Au/sHAPs_300_O_2 and Au/sHAPs_300_H_2 were evaluated by diffuse reflectance

infrared Fourier transform (DRIFT) spectroscopy using CO as a probe molecule. When compared the Au/sHAPs_300 catalysts heat-treated under the same atmosphere (O_2 or H_2), the cationic properties of Au were enhanced as the Au particle size decreased. When compared with the same sHAP support, cationic properties of Au were much more enhanced for Au/sHAP_300_O_2. It is likely that the electronic interaction between Au and the support became stronger as the Au particle size decreased and as the number of surface Au atoms in contact with HAP increased due to SMSI.

We evaluated the catalytic activities of the obtained Au/sHAP catalysts for the isomerization of 34DABE. Fig. 7 shows that the higher the cationic state of Au, the higher the 14DABE yield. In comparison with the same Au/sHAP, Au/sHAP_300_O_2 showed higher catalytic activity than Au/sHAP_300_H_2 despites the fact that the Au particle size was not different. Generally, the formation of SMSI improves thermal stability and durability of metal NP catalysts but shows negative effect on catalytic activity due to a decrease in the number of exposed surface metal atoms. It is worth noting that the enhanced electronic effect of SMSI on Au surpassed the disadvantage of the decrease in the number of active sites. Moreover, the catalyst with SMSI showed no significant deactivation after five recycling tests, indicating that the durability of the catalysts was improved by SMSI.

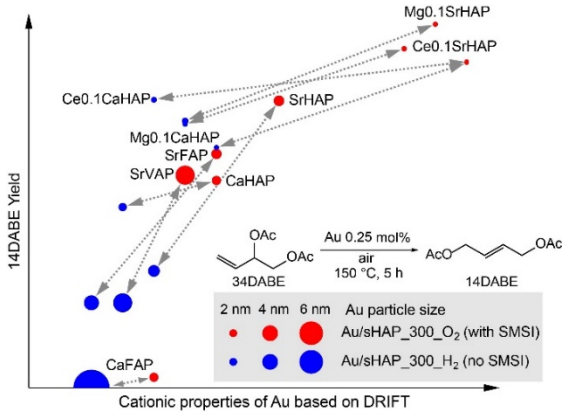


Fig. 7 Relationships between catalytic activity for the isomerizsation of 34DABE to 14DABE and cationic properties of Au for Au/sHAP_300_O_2 with SMSI and Au/sHAP_300_H_2 without SMSI.

■Papers with Peer Review

1. Y. Hirade, T. Ishida, T. Shimada, S. Takagi, *Colloids Surf. A Physicochem. Eng. Asp.*, **624**, 126747-126752(2021).
2. Y. Yoshida, T. Shimada, T. Ishida, S. Takagi, *ACS Omega*, **6**, 21702-21708 (2021).
3. K. Arakawa, T. Shimada, T. Ishida, S. Takagi, *Langmuir*, **37**, 11978–11985 (2021).
4. R. Onishi, K. Sano, T. Shimada, T. Ishida, S. Takagi, *Bull. Chem. Soc. Jpn.*, **94**, 937-942 (2021).
5. Y. Ohsaki, R. Shibatani, T. Shimada, T. Ishida, S. Takagi, *Chem. Lett.*, **50**, 1983-1986 (2021).
6. S. Mathew, A. Sebastian, F. Kuttassery, S. Takagi, H. Tachibana, H. Inoue, *Inorg. Chim. Acta*, **526**, 120529-120539 (2021).
7. K. Arakawa, K. Suzuki, R. Nakazato, Y. Hirade, T. Shimada, T. Ishida, T. Yui, S. Takagi, *Clay Science*, **25**, 27-31 (2021).
8. R. Nakazato, Y. Kou, D. Yamamoto, T. Shimada, T. Ishida, S. Takagi, H. Munakata, K. Kanamura, H. Tachibana, H. Inoue, *Res. Chem. Intermed.*, **47**, 269–285 (2021).
9. A. Waheed, X. Wang, N. Maeda, D. M. Meier, T. Ishida, T. Murayama, M. Haruta, A. Baiker, *Catal. Commun.*, **148**, 106183-106189 (2021).
10. S. Chen, A. M. Abdel-Mageed, A. Hauble, T. Ishida, T. Murayama, M. Parlinska-Wojtan, R. J. Behm, *Appl. Catal. A: Gen.*, **624**, 118318-118327(2021).
11. S. Chen, A. M. Abdel-Mageed, C. Mochizuki, T. Ishida, T. Murayama, J. Rabeah, M. Parlinska-Wojtan, A. Brückner, R. J. Behm, *ACS Catal.*, **11**, 9022–9033(2021).
12. T. Fujita, M. Zysman, D. Elgrabli, T. Murayama, M. Haruta, S. Lanone, T. Ishida, J. Boczkowski, *Sci. Rep.*, **11**, 23129-23138(2021).
13. M. Oshima, K. Sano, Y. Hirade, R. Nakazato, T. Ishida, T. Shimada, S. Takagi, *J. Phys. Chem. Solids*, **161**, 110423-110428(2022).
14. H. Takimoto, Y. Hirade, T. Shimada, T. Ishida, S. Takagi, *Results Chem.*, **4**, 100271-100275(2022).
15. L. X. Dien, H. D. Chinh, N. K. Nga, R. Luque, S. M. Osman, L. G. Voskressensky, T. D. Lam, T. Ishida, T. Murayama, *Mol. Catal.*, **518**, 112053-112057(2022).

■Reviews

1. C–H Bond Functiionalization Using Pd- and Au-Supported Catalysts with Mechanistic Insights of the Active Species, T. Ishida・Z. Zhang・H. Murayama・E. Yamamoto・M. Tokunaga, Synthesis, **53**, 3279–3289 (2021).

■Books

See the annual report in Japanese (3 articles)

■Invited Lectures

1. Nano-structure Controlled Nanosheet-dye Complexes and their Utilization for Photochemical Reactions, S. Takagi (T. Shimada, T. Ishida), Asian photochemistry conference 2021, Invited, Online, Octber-November, 2021.
2. Unique photochemical properties of dyes on the inorganic nanosheets, S. Takagi, (K. Arakawa, T. Shimada, T. Ishida), 2021 International Chemical Congress of Pacific Basin Societies (PACIFICHEM 2021), Invited, Online, December, 2021.
3. The effect of flat inorganic surface on the photochemical properties and reactions of molecules, S. Takagi (T. Shimada, T. Ishida), Saturday Seminar Series (Hosted by Professor V Ramamurthy), Invited, Online, March, 2022.

■Academic Meeting

＊International

1. “In-water” Dehydration reaction of Aromatic Diol on Saponite Surface, K. Arakawa, T. Shimada, T. Ishida, S. Takagi, Asian photochemistry conference 2021, Online, Octber-November, 2021.

＊Domestic

See the annual report in Japanese (40 articles)

■Awards

1. The Best Presentation Award for Students, Annual Meeting on Photochemistry 2021, Ryosuke NAKAZATO (D3), September, 2021.
2. Excellent Presentation Award, 64th Annual Meeting of The Clay Society of Japan, Kyosuke ARAKAWA (D2), September, 2021.
3. The Best Presentation Award, Symposium on Molecular Photo-Functionalities 2021, Kensuke IIKURA (M2), December, 2021.
4. The Best Presentation Award, Symposium on Molecular Photo-Functionalities 2021, Ryota SHIMADA (M1), December, 2021.
5. The Best Presentation Award, Symposium on Molecular Photo-Functionalities 2021, Emiko NAKAYAMA (B4), December, 2021.

Analytical Chemistry Laboratory

■**Members**
Hizuru NAKAJIMA
Associate Prof. / Dr.Eng.
Analytical Chemistry, Micro-TAS, Chromatography, Electrophoresis, Chemical sensor, Bio sensor
room: 9-343 TEL: +81-42-677-1111 Ext.4882
e-mail: nakajima-hizuru @tmu.ac.jp

Shungo KATO
Associate Prof. / Dr.Eng.
Atmospheric Chemistry, Analytical Chemistry, Geochemistry
room: 9-338 TEL: +81-42-677-1111 Ext.4875
e-mail: shungo @tmu.ac.jp

Sifeng MAO
Assistant Prof. / Dr.Eng
Analytical Chemistry, Micro-TAS
room: 9-344 TEL: +81-42-677-1111 Ext.4883
e-mail: maosifeng @tmu.ac.jp

Hidetaka NORITOMI
Assistant Prof. / Dr.Eng.
Biotechnology, Chemical Engineering, Colloid Chemistry
room: 9-148 TEL: +81-42-677-1111 Ext.4838
e-mail: noritomi @tmu.ac.jp

Yoshinori INOUE
Tech. Assistant
room: 9-290 TEL: +81-42-677-1111 Ext.4872
e-mail: inoue-yoshinori @ jmj.tmu.ac.jp

Haruko MIYAMOTO
Tech. Assistant
room: 9-291 TEL: +81-42-677-1111 Ext.4873
e-mail: miyamoto-haruko @jmj.tmu.ac.jp

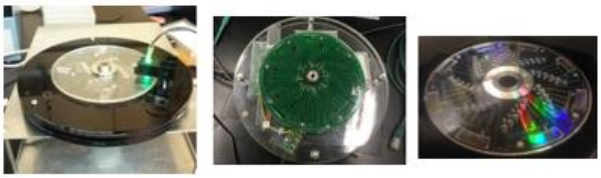
Doctor's course -3
Master's course -12
Bachelor 4 -7
Research student-2

■Outlines of the Research

1. Development of Micro Total Analysis System Using a Compact Disk-type Microfluidic Device

Hizuru NAKAJIMA

We have developed a flow-based ELISA system using a microfluidic device. However, many pumps and valves are required for multiple immunoassays, which affect total size of the analytical system. In this study, we developed a solution sending method based on the centrifugal force generated by rotating a compact disk-type microfluidic device. A portable fluorescence detection system, electrochemical detection system and surface plasmon resonance sensor using the compact disk-type microfluidic device were developed. Since these systems do not need pumps and valves, these systems would be useful for on-site analysis, such as environmental monitoring, food safety testing and point-of-care testing.



2. Development of Portable ELISA System Using Pipette Tips

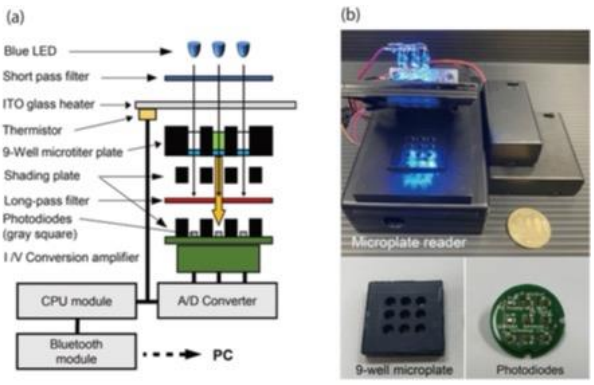
Hizuru NAKAJIMA

Enzyme-linked immunosorbent assay (ELISA) is an immunological assay commonly used to measure antibodies, antigens, proteins and glycoproteins in biological samples. However, the conventional ELISA method relatively needs a long analysis time and many expensive reagents. In addition, commercially available microplate readers are large-size and very expensive. Therefore, it is not possible to measure biological samples and environmental samples in the field by ELISA. To overcome these drawbacks, we developed an ELISA method using pipette tips (PT-ELISA) and the palm-sized fluorescence detector for PT-ELISA. This PT-ELISA system was successfully used in the determination of IgA in human saliva, a marker of stress.

3. Development of Portable Genetic Testing System Based on LAMP

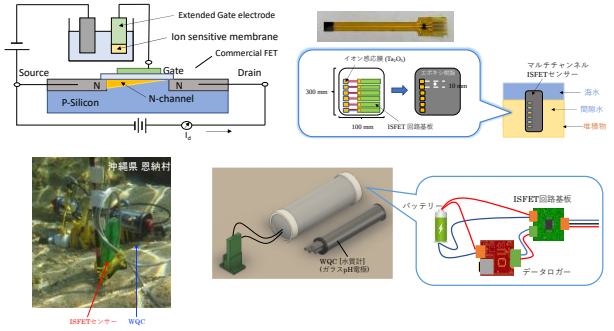
Hizuru NAKAJIMA

A genetic amplification method using polymerase chain reaction (PCR) is commonly used in the genetic test. However, the PCR method is not suitable for on-site genetic test since the method needs large-sized and expensive assay devices such as a thermal cycler, an electrophoresis equipment and an absorption / fluorescence detector. To overcome these drawbacks, a portable genetic testing system based on LAMP was developed using LEDs, photodiodes a transparent glass heater and so on. The genetic testing system was successfully used in the variety identification of rice.



4. Development of Multichannel ISFET Sensor for Measuring pH Distribution of Interstitial Water in Marine Sediment
Hizuru NAKAJIMA

Recentry, marine acidification is progressing with increasing the concentration of CO_2 in atmosphere. Since the marine acidification causes the dissolution of sandy soil in coral reef area, the effect of ocean acidification on marine organisms living in there is apprehended. Therefore, the measurement of pH distribution of interstitial water in marine sediment is important task for evaluating the effect of marine acidification on ecosystem. In general, the pH value of interstitial water in marine sediment is measured by diver using the pH meter with glass electrode. However, the measurement work is very hard, the glass electrode is fragile, and the pH distribution of interstitial water could not be measured at same time. To overcome these drawbacks, a novel multichannel ISFET sensor using Ta_2O_5 as an ion sensitive membrane was developed for measureing the pH distribution of interstitial water in marine sediment.



5. Measurements of VOCs at urban and suburban sites
Shungo KATO

Volatile Organic Compounds (VOCs) were observed at uburban site (Minamiosawa, Koto-ku, Kyoto). Emission sources, contribution to ozone formation of each VOC were estimated. Test measruemnts of ambient air by SIFT-MS was conducted.

6. Atmospheric trace species measurements at remote sites
Shungo KATO

Atmospheric carbon monoxide, ozone, various volatile organic compounds, and hydrogen were continuously observed at remote sites: cape Hedo in Okinawa, Suzu in Ishikawa.

7. Measurements of atmospheric pollutants at mountain sites
Shungo KATO

Carbon monoxide, ozone, and sulferdioxide were observed at the top of Mt. Fuji and the foot of Mt. Fuji (Tarobo observation site). Clear diurnal cycle caused by air motion were observed. Volcanic gas from Mt. Asama to Tarobo was observed.

8. Development of volcanic gas monitoring system using small gas sensor
Shungo KATO

Realtime measurement of volvanic gas at the top of Mt. Fuji during winter without commercial electric power was donducted with low power gase sensor and LPWA ELTRES (SONY). Also, measuremnent of volcanic gases using a portable system was conducted at trails of Mt. Fuji and Owakudani, Hakone volcano.

9. Hydrogen measurement in ambient aire
Shungo KATO

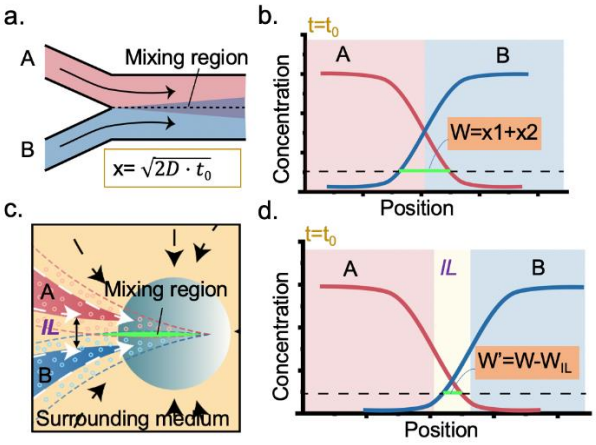
Gas chromatgrapy/Redection gas detector system was constructed for low level hydrogen measuremtns. Atmospheric hydrogen concentration in suburban, urban, and remote sites were observed. Measeruemts on tunnels to observe car exhaust were conducted.

10. Development of microchemical pen and its applications
Sifeng MAO

Micro-chemical pen (MCP), developed by our research group, represents a novel versatile tool for nanowires fabrication. MCP has been proven successful in generating silver nanowires, however, the performance of nanowire fabricated by MCP in sensing chemical/biological species never been investigated. them difficult to use in nano-sensors. For a nanowire to be used in a sensor, long nanowires would be more competitive. The selective fabrication of highly ordered nanowires with high aspect ratios was of low reproducibility, which remains a challenge for laboratory research. Moreover, the mechanism and the fabrication of gold nanowires are still in progress.

11 Insight into micro-chemical pen: microfluidic mechanism for high-resolution surface processing
Sifeng MAO

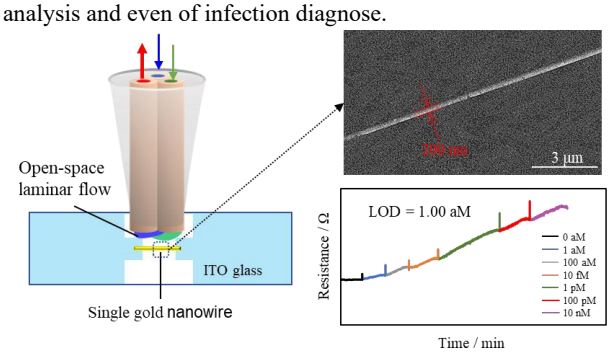
In this study, we have confirmed the existence of an intermediate layer when MCP is working, which provides MCP with extra advantages in surface processing over the conventional open-space microfluidic systems. The variation of the size of IL caused by adjusting relative parameters is further proved to be an important factor for controlling the working area. Although the relationship between the IL and mixing region has not been constructed in fluorescence experiments, the consistence we found between the proposed working principle of IL and the numerical simulation results is enough to explain how much the IL plays a role in the outstanding works of MCP.



12 Regioselective fabrication of gold nanowire using open-space laminar flow for attomolar protein detection
Sifeng MAO

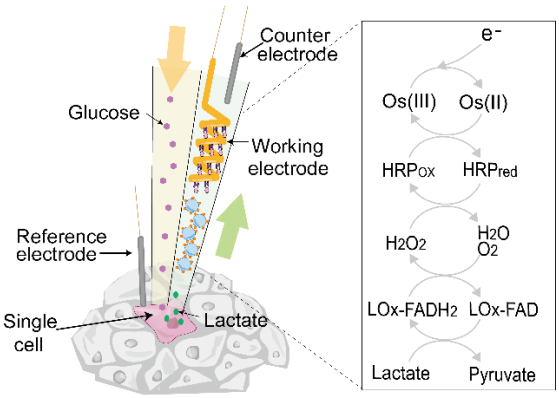
We present an open-space laminar flow approach for fabricating single gold nanowire in a regioselective manner for the first time. This method enabled us to fabricate gold nanowires with the widths ranged of a tens of nanometer to a few micrometers at targeted locations. The gold nanowires were composed of multiple nanoparticles aggregated into a wire-like structure. Due to the structure, a highly sensitive biosensor was successfully realized as sensitive as 1 aM IgA using this single

gold nanowire. The high-performance IgA detection was achieved using a single gold nanowire in this study, however, by changing the modification of the gold nanowires according to the target substance, we expect to develop a sensor that can measure various substances with high sensitivity in the field of pharmacology, medical care, food analysis, environmental analysis and even of infection diagnose.



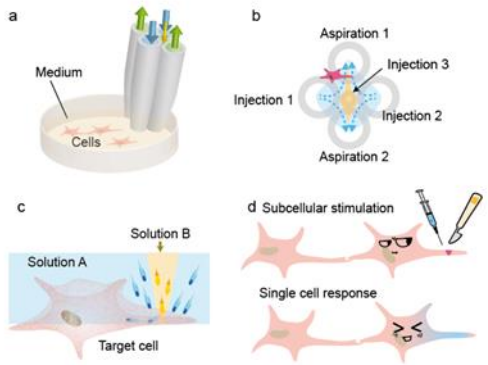
13. Push-pull nozzle system for electrochemical detection of lactate from single cell
Sifeng MAO

In this study, we have presented a new method for the noninvasive, instant, high spatial resolution detection of lactate from single cells. This work involved the use of an in situ electrochemical detection system based on push-pull nozzle system that was developed in this laboratory. Its unique flow system and two-step enzyme transfer measurement enabled us to stably and accurately detect the release of lactate from a single cell. Single cell heterogeneity was successfully monitored in real time and in situ, without any invasive sample treatment. A distinct difference in lactate concentration between single cells was found, indicating that different pathways might be involved in lactate metabolism, which was an often-neglected part of previous studies of tumor microenvironments. Our method provides a new approach for analysing some of the components from a single cell, is potential for understanding of cell heterogeneity.



14. *In situ* subcellular processing program for single cell analysis by open microfluidic probe
Sifeng MAO

In this study, a new open microfluidic probe was used to explore the communication between cells by precise manipulation of a part of the cell. By controlling the fluid velocity at each nozzle, a thin effective region was formed in the central region of the probe. The fluid in the effective region was stable and had high spatial resolutions enough to stimulate and operate a limited region of a single cell without affecting the other parts. The calcium transport was observed from high calcium concentration cells by L-type calcium channel stimulation to the connected cells. Thus, the open microfluidics would provide a new method for cell-to-cell signaling studies, development study of networking, and can also be useful for disease treatment.



15. Application of biochar to stress tolerance of enzymes
Hidetaka NORITOMI

To reduce greenhouse gas emissions, biochar was prepared from forestry residues, which are carbon neutral, and was used as an enzyme carrier. We found that biochar imparts high heat stress tolerance and organic solvent stress tolerance to enzymes. This result would be expected to the applications to bioprocesses such as bioreactors, biosensors, and biofuel cells.

■Papers with Peer Review

1. Q. Zhang, S. Feng, L. Lin, S. Mao, Z. Li, J.-M. Lin
Emerging open microfluidics for cell manipulation
Chemical Society Reviews, 2021, 50, 5333-5348
2. Kenji Morita, Kazuhiro Morioka, Hizuru Nakajima, Katsumi Uchiyama, Akio Yanagida, Atsushi Shoji
Film-Thickness-Controllable System for Preparing Silver Nanofilms through Absorbance Monitoring of the Thickness during a Silver-Mirror Reaction
Analytical Sciences, 2021,37,4,625-631
3. Zhou Lin, Kasai Nahoko, Nakajima Hizuru, Kato Shungo, Mao Sifeng, Uchiyama, Katsumi
In situ single cell stimulation and real-timeelectrochemical detection of lactate response using microfluidic probe
Analytical Chemistry 2021,93,8680-8686
4. Xinning He, Tsuguhiro Kaneko, Huan Luo, Hang Cong, Hizuru Nakajima, Hulie Zeng
A simple and efficient approach to sensitize the fluorescence detection to microwell plate
Sensors and Actuators B: Chemical, 343 130070-130070
5. Sifeng Mao, Xiaohong Hu, Yumi Tanaka, Lin Zhou, Chenhan Peng, Nahoko Kasai, Hizuru Nakajima, Shungo Kato, Katsumi Uchiyama
A chemo-mechanical switchable valve on microfluidic chip based on a thermally responsive block copolymer
Chinese Chemical Letters, In press
6. Kojiro Shimada, Manatsu Mizukoshi, Chak K.Chan, Yong Pyo Kim, Neng-Huei Lin, Kazuhide Matsuda, Syuichi Itahashi, Yoshihiro Nakashima, Shungo Kato, Shiro Hatakeyama
Disentangling the contribution of the transboundary out-flow from the Asian continent to Tokyo, Japan
Environmental Pollution, 286, 117280, 2021
7. J. Chen, S. Mao, Z. He, L. Yang, J. Zhang, J.-M. Lin, Z.-X. Lin
Proteomic Distributions in CD34+ Microvascular Niche Patterns of Glioblastoma

Journal of Histochemistry & Cytochemistry, 2021, 70, 99-110

8. Jiaru Lia, Nanase Kohnoa, Yosuke Sakamoto, Yukiko Fukusaki, Yuka Kousa, Yasuhiro Sadanaga, Yoshihiro Nakashima, Kei Sato, Sathiyamurthi Ramasamy, Akinori Takami, Ayako Yoshino, Tomoki Nakayama, Shungo Kato, Natsuki Ono, Jun Zhoua, Yu Bai, Yoshizumi Kajii
   A quantitative understanding of total OH reactivity and ozone production analysis in a coastal industrial area during AQUAS–Yokohama campaign in summer 2019
   Atmospheric Environment, 267, 2021, 118754
9. Kazuhiro Morioka, Moeko Osashima, Nao Azuma, Kuizhi Qu, Akihide Hemmi, Atsushi Shoji, Hiroya Murakami, Norio Teshima, Tomonari Umemura, Katsumi Uchiyama, Hizuru Nakajima
   Development of a fluorescence microplate reader using an organic photodiode array with a large light receiving area
   Talanta, 238, 122994-122994
10. Ryo Ishii, Kazuhiro Morioka, Takuya Mizumoto, Natsumi Yamasaki, Akihide Hemmi, Atsushi Shoji, Hiroya Murakami, Norio Teshima, Tomonari Umemura, Katsumi Uchiyama, Hizuru Nakajima
    Development of Portable Fluorescence Microplate Reader Equipped with Indium Tin Oxide Glass Heater for Loop-mediated Isothermal Amplification
    Sensors and Materials, Vol. 34, No. 3 (2022) 971–985
11. Atsushi Shoji, Miyu Nakajima, Kazuhiro Morioka, Eiji Fujimori, Tomonari Umemura, Akio Yanagida, Akihide Hemmi, Katsumi Uchiyama, Hizuru Nakajima
    Development of a surface plasmon resonance sensor using an optical fiber prepared by electroless displacement gold plating and its application to immunoassay
    Talanta, 240, 123162-123162

See the annual report in Japanese (2 articles)

■Invited Lectures

■Academic Meeting

＊International

＊Domestic

■Books

1. Hidetaka Noritomi
Promotion in refolding and heat stress tolerance of proteins by adsorption immobilization to biochar
New Frontiers in Medicine and Medical Research Vol. 6, Ed by Syed A. A. Rizvi
Book Publisher International, London, United Kingdom, Chapter 3, (2021) 9-20

2. Hidetaka Noritomi
Application of ionic liquids to enzyme stabilizers for the heat stress tolerance of enzymes
Highlights on Medicine and Medical Research Vol. 11 Ed **by** Dharmesh Chandra Sharma
Book Publisher International, London, United Kingdom, Chapter 12, (2021) 92-103

■Awards

Shishido Laboratory

■**Members**
Tetsuya Shishido
Professor /Dr. Eng.
Catalyst Science, Surface chemistry, Solid acid-base, Selective oxidation, in-situ observation
room:9-551 TEL: +81-42-677-2852 (Ext. 4961)
e-mail: shishido-tetsuya@tmu.ac.jp

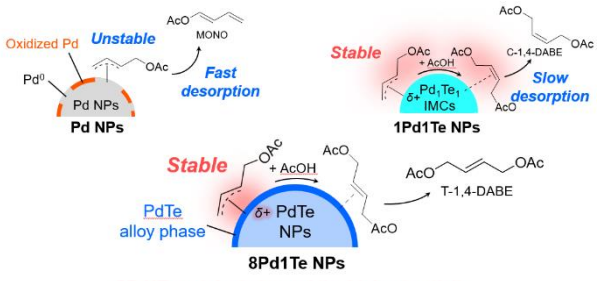
Hiroki Miura
Associate Professor /Dr. Eng.
Catalysis Science, Solid acid-base, Organic chemistry, Organometallic chemistry
room:9-550 TEL: +81-42-677-2851 (Ext. 4962)
e-mail: miura-hiroki@tmu.ac.jp

PD -2
Doctor's course -1
Master's course -12
Bachelor 4 -7

■Outlines of the Research

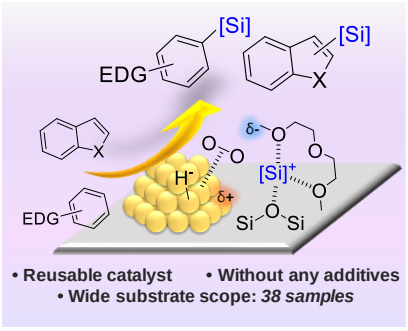
Sstructural analysis of supported Pd-Te catalyst effective for oxidative diacetoxylization of olefins

1,4-butandiol (1,4-BDO) is used as a raw material for various compounds and is industrially produced by diacetoxylation of 1,3-butadiene (1,3-BD) by supported Pd catalyst, followed by hydrogenation and hydrolysis. The most difficult step is diacetoxylation of 1,3-BD, and thus novel catalyst with improved activity and selectivity is required. In this study, the alloying effect of Te on Pd was investigated in detail. Various characterizations revealed that changes in the structure of the supported metal species affect the catalytic activity in addition to the interaction between Pd and Te. It was found that the highly active catalyst maintained the fcc structure of Pd and selectively formed the PdTe alloy on the surface, which facilitated the interaction with the substrate 1,3-BD, and stabilized the intermediate.



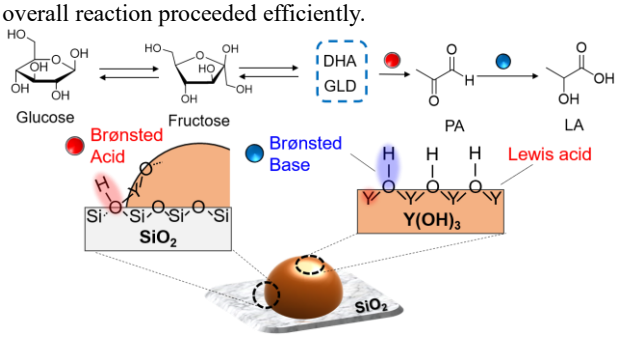
High-efficiency silylation of sp^2 C–H bonds with supported Au catalysts

Heterogeneous gold-catalyzed C(sp^2)–H silylation is developed. A variety of heteroarenes and electron-rich arenes participated in gold-catalyzed silylation to afford the corresponding heteroaryl and arylsilanes in good to excellent yields. A detailed mechanistic investigation corroborated that the cooperative catalysis of ether and O_2-activated gold nanoparticles realized heterolysis of the Si–H bond to generate silyl cations, which enabled subsequent electrophilic C–Si bond formation. The high activity, reusability and environmentally-friendly nature of the heterogeneous gold catalysts as well as the scalability of the reaction system realize the sustainable synthesis of aryl and heteroarylsilanes.



Lactic acid production from glucose over Y_2O_3-based catalysts under base-free conditions

Methods to catalytic conversion of glucose into lactic acid (LA), which is a versatile platform chemical, have been widely investigated. Herein, a variety of metal oxide catalysts were used for lactic acid (LA) production from glucose under strong homogeneous base-free conditions. Among the metal oxides tested, Y_2O_3 afforded LA in moderate yield together with trioses (dihydroxyacetone and glyceraldehyde) and fructose. It was found that the Y_2O_3/SiO_2 catalyst can effectively catalyze the transformation of glucose into LA. Compared to Y_2O_3, the LA yield was remarkably improved. The characterization results showed that $Y(OH)_3$ was highly dispersed on the Y_2O_3/SiO_2 catalyst, acting as a Brønsted base and promoting LA formation from pyruvaldehyde (PA). Brønsted acid sites (hydroxyl groups) located at the interface between $Y(OH)_3$ and SiO_2 promoted the dehydration of trioses to form PA. The acid and base sites on the Y_2O_3/SiO_2 catalyst functioned in concert to ensure that the overall reaction proceeded efficiently.



■Papers with Peer Review

1. Gold-Catalyzed Thioetherification of Allyl Benzyl and Propargyl Phosphates Miura, H.; Toyomasu, T.; Nishio, H.; Shishido, T. *Catal. Sci. Technol.* **2022**, *12*, DOI: 10.1039/D1CY02085D
2. Deposition of Highly Dispersed Gold Nanoparticles onto Metal Phosphates by Deposition-Precipitation with Aqueous Ammonia Nishio, H.; Miura, H.*; Kamata, K.; Shishido, T. *Catal. Sci. Technol.* **2021**, *11*, 7141–7150.
3. Electrophilic C(sp^2)-H Silylation by Supported Gold Catalysts Miura, H.; Hirata, R.; Toyomasu, T.; Shishido, T. *ChemCatChem* **2021**, *13*, 4705–4713. ***【Featured as a Front Cover】 【Highlighted in ChemistryViews 2021.】***

4. Selective catalytic oxidation of ammonia to nitrogen over zeolite-supported Pt-Au catalysts: Effects of alloy formation and acid sites Wang, H.; Lin, M.; Murayama, T.; Feng, S.; Haruta, M.; Miura, H.; Shishido, T. *J. Catal.* **2021**, *402*, 101–113.
5. Ag size/structure-dependent effect on low-temperature selective catalytic oxidation of NH_3 over Ag/MnO_2 Wang, H.; Lin, M.; Murayama, T.; Feng, S.; Haruta, M.; Miura, H.; Shishido, T. *ACS Catal.* **2021**, *11*, 8576–8584.
6. Lactic acid production from glucose over Y_2O_3-based catalysts under base-free conditions Hata, D.; Aihara, T.; Miura, H.; Shishido, T. *J. Jpn. Petrol. Inst.* **2021**, 64, 280–292.
7. High-density formation of metal/oxide interfacial catalytic active sites through hybrid clustering, Hayashi, S.; Shishido, T. *ACS Applied Materials & Interfaces*, 2021, 13, 22332–22340.
8. Isotopic $^{18}O/^{16}O$ Substitution Study on the Direct Partial Oxidation of CH_4 to Dimethyl Ether over a Pt/Y_2O_3 Catalyst Using NO/O_2 as an Oxidant, Ghampson, I. T.; Lundin, S.-T. B.; Shishido, T.; Oyama, S. T. *Catal. Sci. Technol.* **2021**,11, 2708–2712.
9. Metal–support cooperation in $Al(PO_3)_3$-supported platinum nanoparticles for the selective hydrogenolysis of phenols to arenes Jin, X.; Tsukimura, R.; Aihara, T.; Miura, H.; Shishido, T.; Nozaki, K. *Nat. Catal.* **2021**, *4*, 312–321. ***【Featured as a Front Cover】***

■Invited Lectures

1. Switching the Selectivity of CO2 Hydrogenation Over Supported Rh Catalysts Tetsuya Shishido, Kazuma Fukuda, Junpei Suzuki, Hiroki Miura, The Second International Symposium of Young Scholar on Carbon Resources Conversion, Oct. 15, 2021, Bangkok, Thailand
2. Design of supported palladium-gold alloy catalysts for highly efficient hydrogen storage systems
   Tetsuya Shishido, Hiroki Miura, The international Chemical Congress of Pacific Basin Societies 2021(Pacifichem 2021, Virtual), Dec. 16-21, 2021, Online
3. Borylation of sp3 C-O bonds under heterogeneous gold catalysis H. Miura, The 2nd International Electronic Conference on Catalysis Sciences (ECCS2021), October 27, 2021, Online
4. Switching the Selectivity of CO2 Hydrogenation Over Supported Rh Catalysts, Tetsuya Shishido, Kazuma Fukuda, Junpei Suzuki, Hiroki Miura, , The international Chemical Congress of Pacific Basin Societies 2021(Pacifichem 2021, Virtual) Dec. 16-21, 2021, Online

■Academic Meeting

＊Domestic

See the annual report in Japanese (25 articles)

■Awards

1. Poster Award "C-H silylation of indoles by supported Au catalysts" Tomohiro Tanaka 18th Workshop on Catalysis science (16-18 September 2021, online).
2. Poster Award "Effect of phosphrous addition on CO2 hydrogenation by supported Rh catalysts" Kazuma Fukuda 18th Workshop on Catalysis science (16-18 September 2021, online).

ShudoLaboratory

■Members

Toshio Shudo
Professor /Dr. Eng.
Energy Engineering, Thermal Engineering, Automotive Engineerng, Hydrogen Energy
room:9-455 TEL: +81-42-677-2715
e-mail: shudot@tmu.ac.jp

Doctor's course -2
Master's course -6
Bachelor 4 -3

■Outlines of the Research

1. Performance improvement in polymer electrolyte fuel cell.
Because polymer electrolyte fuel cell has higher energy efficiency and lower power density compared to internal combustion engine, it is important to improve the performance of polymer electrolyte fuel cell. This research investigates the effect of porous metal flow field for even supply of reactants to the whole area of electrodes.

2. Performance improvement in direct methanol fuel cell.
Direct methanol fuel cell system has higher energy density and lower power density compared to polymer electrolyte fuel cell system. This research investigates the effect of porous metal flow field for enhancing the reactant supply and product removal at the electrodes.

3. Ignition control in homogeneous charge compression ignition combustion.
Internal combustion engine has higher power density and lower energy efficiency compared to fuel cell system. This research investigates a new combustion system by the compression ignition of homogeneous fuel-air mixture for achieving higher thermal efficiency in internal combustion engines.

■Book Chapter

See the annual report in Japanese

■Review

See the annual report in Japanese

■Academic Meeting

＊Domestic

See the annual report in Japanese

■Awards

See the annual report in Japanese

Applied Chemistry Colloquium

393rd 2021/9/14

Takeshi Serizawa (Tokyo Institute of Technology)

" Functional polymer materials by biomimetic properties"

394th 2021/12/3

Toshio Kamiya (Tokyo Institute of Technology)

" New material design utilizing chemistry and computational science"

395th 2021/12/7

Hideo Hosono (Tokyo Institute of Technology)

" From molecular chemistry towards condensed matter science"

396th 2021/12/23

Masamichi Yamanaka (Meiji Pharmaceutical University)

" Creation of supramolecules by molecular design of urea derivatives"

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