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 2023

Department of Applied Chemistry for Environment

Reports from Research Groups

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Doctor's course - 4
Master's course - 19
Bachelor 4 - 11
Researcher - 3

■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 conducted investigations using SAXS and other methods on the gas permeation mechanism of composite membranes with newly developed surface-modified silica nanoparticles added, as well as the mechanism by which toughness is not reduced. It was suggested that the structure of particle clusters is important for the manifestation of material properties.

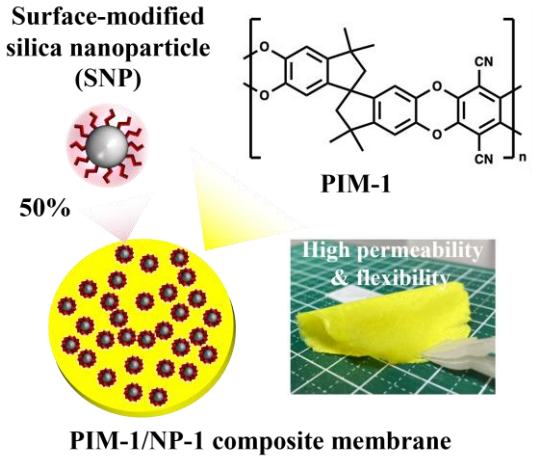

Figure 1. Schematic drawing of nanoparticle/PIM-1 composite membrane.

2. Study of Polymer Electrolyte Membrane

Hiroyoshi KAWAKAMI, Manabu TANAKA, Masafumi YAMATO, Kiyoshi SATO, Yasuyo OGINO

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, novel nanofiber composite membranes were fabricated to improve proton conductivity. Blend nanofibers consisting of polybenzimidazole and sulfonate poly(arylene ether sulfone) (SPAES) were fabricated. After doping with phytic acid, the nanofibers were composed with Nafion to yield nanofiber composite membranes. It was revealed that the composite membrane using SPAES with higher sulfonic acid contents showed improved proton conductivity. Development of novel nanofiber composite membranes using novel sulfonated polymers as nanofibers and matrix polymer electrolytes were also investigated. Radical quenchers to improve membrane stabilities were also developed.

Another study on water electrolysis using anion exchange membranes and anion exchange ionomers were also carried out.

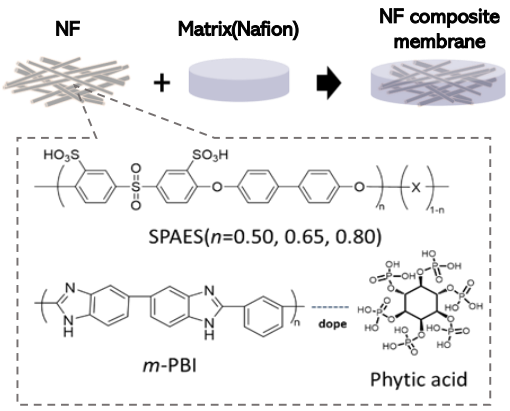

Figure 2. Fabrication of blend polymer nanofiber composite membranes consisting of SPAESs with different sulfonic acid contents for fuel cell applications.

3. Study of Electrospun Nanofibers

Hiroyoshi KAWAKAMI, Manabu TANAKA, Yasuyo OGINO

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 developed polymer nanofiber composite membranes for all solid state secondary batteries. The nanofiber composite membranes consisted of poly(ethylene oxide) (PEO)-based matrix electrolytes with different lithium salt concentrations were fabricated. The nanofiber composite membranes, especially with low lithium ion concentration, showed high ion conductivity and lithium transference number by composing with nanofibers.

Another study on rechargeable zin air batteries using anion conductive nanofiber-based gel polymer electrolyte membranes were also carried out.

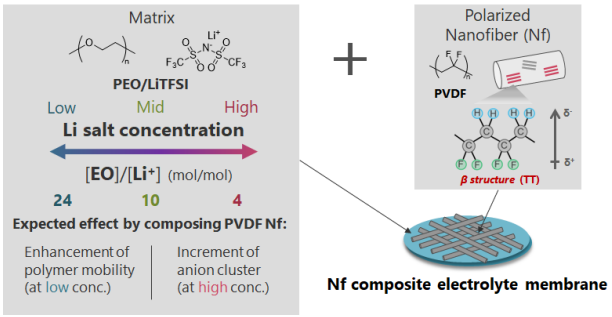

Figure 3. Fabrication of nanofiber composite membranes consisting of polymer matrix electrolytes with different lithium salt concentrations for all-solid-state lithium ion batteries.

4. Epigenetics Engineering for Cancer Therapy

Hiroyoshi KAWAKAMI, Kiyoshi SATO, Masahiro YOSHIOKA

Epigenetics is a system to control the ON/OFF switch of gene expression without altering the DNA base sequence, and maintains the changes after cell division. Many diseases, including cancer, are strongly associated with epigenetic abnormalities. However, epigenomic alterations are reversible and therefore can be reversed artificially, resulting in providing a new therapeutic method.

To expand the therapeutic range of epigenetics-controlled nanocarriers that can co-deliver three epigenetic drugs, the apoptosis- and cellular senescence-inducing effects were tested in various type of cancer cells. Similar effects were confirmed against multiple cancer cells, indicating the generality of the therapeutic effects of the epigenetics-controlled nanocarriers.

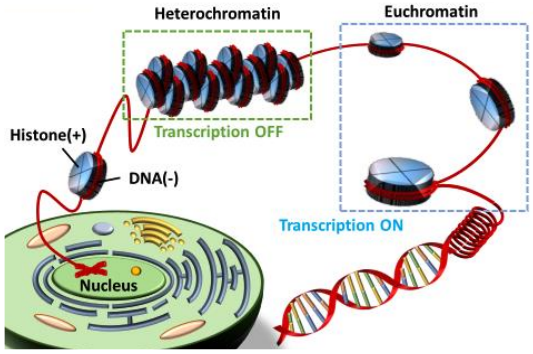

Figure 4. Gene expression control through chromatin modifications.

5. Suppression of Cellular Senescence

Hiroyoshi KAWAKAMI, Kiyoshi SATO, Masahiro YOSHIOKA, Keisuke ASHIBA

Although cellular senescence functions as a tumor-suppressive mechanism, the accumulation of senescent cells in various tissues causes age-related diseases such as diabetes and Alzheimer's disease. Moreover, the cytokines and chemokines secreted by senescent cells affect neighboring cells. Cellular senescence is also a major factor in quality deterioration of the source cells. Therefore, suppression of cellular senescence of stem cells and immune cells during *in vitro* expansion is one of the most important issues for the prevalence of regenerative medicine and cell-based therapy.

In this year, we investigated that reactivation of mitophagy in early- and late-passage mesenchymal stem cells and long-term cultured T cells by mitophagy-induced liposomal nanocarriers (M-NC). The M-NC removed dysfunctional mitochondria from the senescent cells and restored the cell proliferation ability and cell function. Thus, M-NC will provide new strategies for the *ex vivo* cell expansion for regenerative medicine and cell therapy.

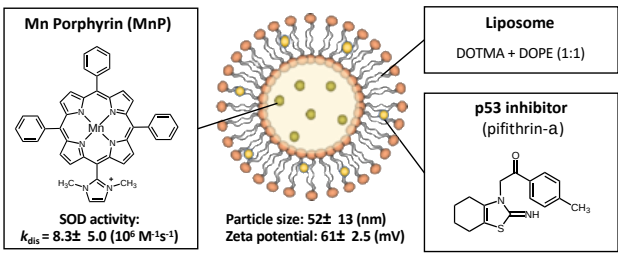

Figure 5. Structure of mitophagy-induced liposomal nanocarrier.

6. Fabrication of Engineering Exosomes

Hiroyoshi KAWAKAMI, Kiyoshi SATO, Masahiro YOSHIOKA

Exosomes are a type of extracellular vesicles with a diameter of 50 to 200 nm, and function as transport carriers for intercellular communications that selectively deliver miRNAs and proteins to target cells. In recent years, its use in cancer diagnosis has been investigated. Research of engineered exosomes is also active due to the excellent biocompatibility and

transport selectivity that can be used as DDS carriers by modifying natural exosomes or by modifying mother cells to produce exosomes with enhanced therapeutic efficacy.

In this year, we investigated the fabrication of engineered exosomes that incorporate drugs or miRNA for the therapy of target cells into exosomes secreted from mesenchymal stem cells and cancer cells. These engineered exosomes are expected to serve as new therapeutic methods and DDS carriers.

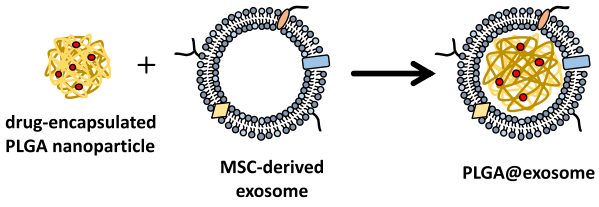

Figure 6. An example for engineering exosome.

7. Processing of feeble magnetic materials under a magnetic field

Masafumi YAMATO

We are conducting research aimed at controlling the higher-order structure skillfully by utilizing the feeble magnetic properties exhibited by many substances, with the goal of improving material characteristics and manifesting novel functionalities. This year, we investigated the magnetic orientation of layered double hydroxide, specifically hydrotalcites. It was revealed that the easy magnetization axis of hydrotalcites varies depending on the constituent metal species. Those containing transition metals exhibiting paramagnetism transitioned to paramagnetic behavior, with the manifestation of magnetic dipole interactions becoming apparent. These findings suggest that new methods of controlling higher-order structures could be provided for the development of composite materials including hydrotalcites.

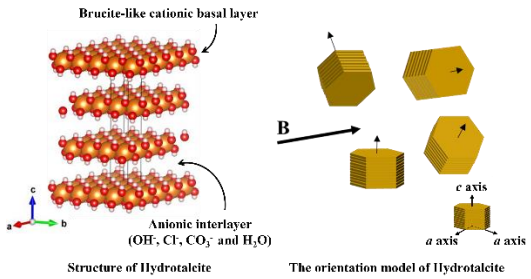

Figure 7. Crystal structure of hydrotalcite (left) and schematic drawing of magnetic orientation (right).

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. Kazuto Suzuki, Manabu Tanaka, Masahiro Kuramochi, Shun Yamanouchi, Noriko Miyaguchi, Hiroyoshi Kawakami, "Development of Blend Nanofiber Composite Polymer Electrolyte Membranes with Dual Proton Conductive Mechanism and High Stability for Next-Generation Fuel Cells", *ACS Applied Polymer Materials*, **5**, 7, 5177-5188 (2023). DOI: https://pubs.acs.org/doi/10.1021/acsapm.3c00656
2. Keisuke Ashiba, Koki Mino, Yui Okido, Kiyoshi Sato, Hiroyoshi Kawakami, "Senescence recovering by dual drug-encapsulated liposomal nanoparticles for large-scale human cell expansion", *Journal of Artificial Organs*, 26, 246-250 (2023). DOI: 10.1007/s10047-022-01356-x
3. Kiyoshi Sato, Hiroyoshi Kawakami, "Mitochondrial Dysfunction and Nanocarrier-Based Treatments in Chronic Obstructive Pulmonary Disease (COPD)", *Oxygen*, **3**, 394-406 (2023). DOI: 10.3390/oxygen3040026
4. Momoka Chatani, Naomi Saito, Masahiro Yoshioka, Yuichi Kinoshita, Hanae Nakamura, Yuki Hashimoto, Akiko Takenouchi, Katsuhiko Yoshizawa, "Pathophysiological effect of acerola in streptozicin-induced cataract rat model", *Functional Food Research*, **19**, 90-99, (2023) (in Japanese).
5. Nagy L. Torad, Yuta Tsuji, Azhar Alowasheeir, Masako Momotake, Kazuki Okazawa, Kazunari Yoshizawa, Michio Matsumoto, Masafumi Yamato, Yusuke Yamauchi, Miharu Eguchi, "Extraordinary Acceleration of an Electrophilic Reaction Driven by the Polar Surface of 2D Aluminosilicate Nanosheets", Small, 2205857 (2023).
6. Yasuko Noritomi, Takashi Kuboki, Hidetaka Noritomi, "Enhancement of catalytic efficiency of enzymatic redox reaction by composing a horseradish peroxidase-modified electrode with ionic liquids", Liquids, submitted.

■Books

1. Manabu Tanaka, Hiroyoshi Kawakami, "Electrospun Sulfonated Polyimide Nanofibers for Polymer Electrolyte Composite Membranes", in "*Polyimides - Advances in Blends and Nanocomposites*", M.-D. Damaceanu, R. N. Darie-Nita, Eds, Chapter 9, pp325-352, Elsevier (2023).
2. Yuri Nara, Hiroyoshi Kawakami, Manabu Tanaka, "Water Electrolysis using Anion Exchange Membranes", in "Recent Trends of Methanation and Green Hydrogen", Yasushi Sekine, Ed, Chapter 7, Section 3, 208-215, CMC Publishing (2023). (in Japanese)
3. Manabu Tanaka, "Tips for Researching Abroad – Let's go abroad for now !", *Sen'i Gakkaishi (Journal of The Society of Fiber Science and Technology, Japan)*, **80**, 1, P2-6 (2024).
4. Hiroyoshi Kawakami, "Polymer Nanofiber Composite Electrolyte Membrane" Journal of the Society of Polymer Science, 72,11, p.p550-552 (2023).
5. Hiroyoshi Kawakami, "CO2 separation using highly permeable polymer membranes," Separation Technology Society Journal, 53,6, 352-359 (2023).
6. Hiroyoshi Kawakami, "Polymer Materials Chemistry for Engineering [Newly Revised Edition]" Science Publishing, 2024 edition.
7. Masafumi Yamato, "Functional Control of Crystalline Polymers Using Magnetic Orientation", in "*Enhancement of Performance through Polymer Crystallization and Stretching*", CMC Publishing, (2024). (in Japanese)
8. Masafumi Yamato, Hiroyoshi Kawakami, "Development of Ultra-High CO_2 Permeable Separation Membranes

Using Nano-Spaces", in "*Recent Trends in Methanation and Green Hydrogen*" CMC Publishing, (2023). (in Japanese)

9. Masafumi Yamato, Kazuma Komine, Kohki Takahashi, Development of organic-inorganic composite materials with high gas permeability II, *2022 Annual report of high field laboratory for superconducting materials in institute for materials research at Tohoku university*, p.p. 161-162 (2023) (in Japanese)

■Invited Lectures

1. Masafumi Yamato, Thermal and magnetic properties of polymer, *2022 Basic seminar of polymer science for young engineers*, Dec. 2023, Tokyo, Japan (in Japanese).
2. Masafumi Yamato and Hiroyoshi Kawakami, Advancing nanoparticle-containing gas separation, International Conference on Nano Research and Development, Dec. 2023 (Singapore)
3. Masafumi Yamato, Towards the realization of CO_2 Direct Air Capture (DAC): the 371st Meeting of the Science and Technology Outlook Conference, Jan. 2024, Tokyo, Japan (in Japanese)
4. Kiyoshi Sato, "Nanocarriers for designer exosomes", COSME Tech 2024 Tokyo (Tokyo), January 2024 (in Japanese).
5. Manabu Tanaka, Water Electrolysis using Anion Exchange Membranes for Green Hydrogen Production, Johokiko Seminar, June 2023, Online (in Japanese).
6. Manabu Tanaka, Anion Exchange Membrane Water Electrolysis: From Fundamentals to State-the-art Research, CMC research webinar, July 2023, Online (in Japanese).
7. Manabu Tanaka, Anion Conductive Polymers for Water Electrolysis, JAIST seminar, August 2023, Ishikawa.
8. Manabu Tanaka, Fuel Cell Applications of Proton Conductive Polymer Nanofiber Frameworks, Topical Seminar, Hydrogenomics Alliance, Japan, October 2023, Online (in Japanese).
9. Manabu Tanaka, Fundamentals and Key Technology of Anion Exchange Membrane Water Electrolysis, Technical Information Institute Seminar, November 2023, Online (in Japanese).
10. Manabu Tanaka, Anion Exchange Membrane Water Electrolysis for Green Hydrogen Production, Johokiko Seminar, December 2023, Tokyo (in Japanese).
11. Manabu Tanaka, Recent Advances on Anion Exchange Membrane Water Electrolysis, 2nd UK-Japan Symposium on Advanced Materials, January 2024, Online.
12. Manabu Tanaka, Organic Nanoionics in Polymers for Energy Conversion System, Chemistry Department Seminar, University of Cambridge, March 2024, Cambridge, UK.
13. Kiyoshi Sato, "Production of functional exosomes using designer cells created by nanocarrier treatment", The 6th Regenerative Medicine Industry-Academia Collaboration Techno Action (Niigata), March 2024 (in Japanese).
14. Masafumi Yamato, "Study in Direct Air Capture", EcoPro 2023 (Tokyo), Dec. 2023.
15. Hiryoshi Kawakami, "Electrolyte membrane initiatives with a view to 2030 and beyondt", Fuel Cell Research Group 158th Seminar (Tokyo), June 2023.
16. Hiroyoshi Kawakami, "Aiming for DAC with polymer membranes - Development of ultra-high CO2 permeation separation membranes-", RITE Industrialization Strategy Council 23rd Seminar, (Online), July 2023.
17. Hiroyoshi Kawakami, "Creation of designer stem cells and their functions of modified exosomes produced", 5th PharmaLab EXPO Tokyo, Tokyo, July 2023.
18. Hiroyoshi Kawakami, "Possibility of DAC using ultra-high CO2 permeability separation membrane", Information Technology Organization Seminar, Tokyo, September 2023.
19. Hiroyoshi Kawakami, "Research and development of new proton-conducting membranes for next-generation fuel cells", 14th New Electrocatalyst Symposium, Shizuoka, October 2023.
20. Hiroyoshi Kawakami, "Polymer Revolution: New Global Warming Countermeasures Opened Up by Mass Transport", Science Techno Frontier Forum at University of Tokyo, Tokyo, March 2024.
21. Hiroyoshi Kawakami, "CO2 separation using highly permeable polymer membranes", 29th Kansai Region Separation Technology Lecture, (held online), March 2024.
22. Hiroyoshi Kawakami, " 2023 NEDO Fuel Cell/Hydrogen Technology Development Roadmap Report Meeting", NEDO, (held online), March 2024.

■Academic Meeting

1. Mizuki Akatsuka, Masafumi Yamato, Hiroyoshi Kawakami. Temperature dependence of gas permeation properties in polymer of intrinsic microporosity (PIM-1): effect of physical aging. 72th SPSI Annual Meeting (G MESSE GUNMA), 100556, May 2023.
2. Kota Nagano, Masafumi Yamato, and Kawakami Hiroyoshi, Pressure dependence of gas permeation properties of surface-modified silica nanoparticle/PIM-1 composite membranes, 72th SPSI Annual Meeting (G MESSE GUNMA), 1Pa061, May 2023 (in Japanese)
3. Natsuki Inoue, Manabu Tanaka, Hiroyoshi Kawakami, Chemical durability evaluation of nanofiber composite membranes for polymer electrolyte fuel cells, The 72th SPSI Annual Meeting (G-Messe Gunma), 3Pb052, May 2023 (in Japanese)
4. Kazuki Takashio, Masafumi Yamato, Hiroyoshi Kawakami, Effect of solvents on asymmetric fluorine-containing polyimide membranes by dry-wet phase inversion process, The 72th SPSJ Annual Meeting (Gunma Convention Center), 1Pb062, May 2023 (in Japanese)
5. Yusuke Fujita, Koki Mino, Keisuke Ashiba, Masahiro Yoshioka, Kiyoshi Sato, Hiroyoshi Kawakami, Production of Designer Stem Cells by Reactivation of Mitophagy, 72th SPSI Annual Meeting (Gunma), May 2023.
6. Ryodai Fujihashi, Manabu Tanaka, Hiroyoshi Kawakami, Fabrication and Conductivity Evaluation of Nanofiber Composite Electrolyte Membranes Consisted of Carbonate-based Solid Polymer Electrolytes, The 72th SPSJ Annual Meeting (Gunma Convention Center), 1Pa053, May 2023 (in Japanese)
7. Yasutaka Kuwahara, Toyotaka Nakae, Hiroyoshi Kawakami, Fabrication of electrolyte composite membranes using PVA nanofiber framework and its fuel cell property, The Annual Meeting of the society of fiber

science and technology Japan (Tower Hall Funabori), 1C08, June 2023 (in Japanese)

8. Natsuki Inoue, Kazuto Suzuki, Manabu Tanaka, Hiroyoshi Kawakami, Fuel Cell Characterization of Nanofiber Composite Electrolyte Membranes with High Proton Conductivity and Durability, The Annual Meeting of the society of fiber science and technology Japan (Tower Hall Funabori), 1C15, June 2023 (in Japanese)
9. Akari Tatsukawa, Toyotaka Nakae, Hiroyoshi Kawakami, Effects of Post-treatment on Fuel Cell Properties of Polymer Nanofiber Composite Membranes, The Annual Meeting of the society of fiber science and technology Japan (Tower Hall Funabori), 1C16, June 2023 (in Japanese)
10. Ryodai Fujihashi, Kenta Sando, Manabu Tanaka, Hiroyoshi Kawakami, Lithium ion conductive characteristics of polymer nanofiber composite electrolyte membranes fabricated from different polymer electrolytes, The Annual Meeting of the society of fiber science and technology Japan (Tower Hall Funabori), 1C04, June 2023 (in Japanese)
11. Masahiro Yoshioka, Hiroyoshi Kawakami, Senescence induction in epigenetically modified cancer cells and alternation of extracellular vesicles, The 27th Annual Meeting of the Japanese Association for Molecular Target Therapy of Cancer (Saga City Cultural Center), P4-02, June. 2023.
12. Hiyori Iitsuka, Shuntarou Kimura, Masayoshi Yoshioka, Kiyoshi Sato, Hiroyoshi Kawakami, Characterization of cancer senescent cells epigenetically modified by functional nanocarriers, The 52nd symposium on medical polymers (Tokyo), July 2023 (in Japanese)
13. Kiyoshi Sato, Ayaka Mori, Koki Mino, Keisuke Ashiba, Masahiro Yoshioka, Hiroyoshi Kawakami, “Exosome-mimicking liposomal nanocarriers for rejuvenation of senescent stem cells”, 13th International Congress on Membranes and Membrane Processes (ICOM 2023) July 2023 (Makuhari Messe)
14. 14. Manabu Tanaka, Hiroyoshi Kawakami, Development of All-Solid-State Lithium Ion Batteries based on Polymer Nanofiber Composite Electrolyte Membranes, 13th International Congress on Membranes and Membrane Process (Makuhari Messe), O1.MF-10, July 2023.
15. Mizuki Akatsuka, Masafumi Yamato, Hiroyoshi Kawakami. Effect of physical aging on the temperature dependence of gas permeation properties of polymer of intrinsic microporosity (PIM-1). 13th International Congress on Membranes and Membrane Process (Makuhari Messe), P2-MH-06, July 2023.
16. Kota Nagano, Masafumi Yamato, and Kawakami Hiroyoshi, Pressure dependence of gas permeation properties of PIM-1 composite membranes loaded with surface-modified silica nanoparticles, ICOM2023 (MAKUHARI MESSE), P2-MX-08, July 2023
17. Natsuki Inoue, Manabu Tanaka, Hiroyoshi Kawakami, Development of nanofiber composite electrolyte membranes with high proton conductivity and durability for fuel cell applications, 13th International Congress on Membranes and Membrane Processes (Makuhari Messe), P2-MF-12, July 2023 (in English)
18. Kazuki Takashio, Masafumi Yamato, Hiroyoshi Kawakami, Effect of solvents on asymmetric polyimide membranes containing surface-modified silica nanoparticles by dry-wet phase inversion process, 13th International Congress on Membranes and Membrane Processes (Makuhari Messe), P2-MX-09, July 2023.
19. Akari Tatsukawa, Toyotaka Nakae, Hiroyoshi Kawakami, Effects of thermal treatment of polymer nanofiber composite membranes on the proton-exchange properties, The 13th International Congress on Membranes and Membrane Processes (Makuhari Messe), P2-MF-13, July 2023.
20. Yusuke Fujita, Koki Mino, Keisuke Ashiba, Masahiro Yoshioka, Kiyoshi Sato, Hiroyoshi Kawakami, Development of mitophagy-inducing nanocarriers for rejuvenation of senescent mesenchymal stem cells, ICOM2023 (Chiba), P1-BD-30, July 2023.
21. Kiyoshi Sato, Hiyori Iitsuka, Haruka Mitome, Masahiro Yoshioka, Hiroyoshi Kawakami, “New strategy for cancer therapy by cell conversion from cancer cells to senescent cells”, 72nd Symposium on Macromolecules, September 2023 (Kagawa Uviv,) (in Japanease)
22. Manabu Tanaka, Yubing Dong, Hiroyoshi Kawakami, Fabrication of Cross-linked Network Polymer Electrolyte Membranes and Their Application to Lithium Ion Batteries, 72nd Polymer Symposium in Japan, 1M15, September 2023 (Kagawa Univ.) (in Japanease).
23. Masahiro Yoshioka, Yusuke Fujita, Kiyoshi Sato, Hiroyoshi Kawakami, Mitophagy-inducing nano-carrier for the production of designer stem cells, The 72th Polymer Symposium in Japan, (Kagawa Univ.), 2Pc89, Sept. 2023.
24. Yuri Nara, Shuhei Koyama, Kento Kasahara, Kensaku Nagasawa, Yoshiyuki Kuroda, Shigenori Mitsushima, Hiroyoshi Kawakami, Manabu Tanaka, Synthesis and water electrolysis application of various anion conductive polyfluorenes with different ion exchange capacities, 72nd Polymer Symposium in Japan, 2M17, September 2023 (Kagawa Univ.) (in Japanease).
25. Mizuki Akatsuka, Masafumi Yamato, Hiroyoshi Kawakami. Gas Permeability Performance of Polymer of Intrinsic Microporosity (PIM-1) at Temperatures Near 100 °C. 72nd Symposium on Macromolecules (Kagawa University), September 2023.
26. Kota Iwasaki, Ryota Inahara, Natsuki Inoue, Akari Tatsukawa, Manabu Tanaka, Hiroyoshi Kawakami, Development of polymer nanofiber-based composite electrolyte membranes and evaluation of the proton conduction mechanism in the composite membranes, The 72th Polymer Symposium in Japan, (Kagawa Univ.), 2M12, Sept. 2023. (in Japanese)
27. Kaito Udo, Mizuki Akatsuka, Masafumi Yamato, Hiroyoshi Kawakami, Property of high gas permeable polymer membranes at high temperature, The 54th SCSJ Autmn meeting (Fukuoka Univ.), PA333, Sept. 2023.
28. Kota Nagano, Masafumi Yamato, and Kawakami Hiroyoshi, CO2 permeation properties of surface-modified nanoparticle/PIM-1 composite membrane at low feed pressure, SCEJ 54th Autumn Meeting (Fukuoka Univ.), K123, Sept. 2023
29. Kota Nagano, Masafumi Yamato, and Kawakami Hiroyoshi, Pressure dependence of gas permeation of

surface-modified nanoparticle/PIM-1 composite membranes, SCEJ 54th Autumn Meeting (Fukuoka Univ.), PA334, Sept. 2023

30. Yuri Nara, Moe Tomita, Kento Kasahara, Kensaku Nagasawa, Yoshiyuki Kuroda, Shigenori Mitsushima, Hiroyoshi Kawakami, Manabu Tanaka, Synthesis and Water Electrolysis Application of Poly(fluorene) Anion Conductive Polymers, FEMS EUROMAT 2023 (Online Virtual Meeting, Germany), #1663, September 2023.
31. Yasutaka Kuwahara, Miyui Ono, Yuri Nara, Hiroyoshi Kawakami, Manabu Tanaka, Fabrication of Anion Conductive Gel Polymer Electrolyte Membranes and Their Application to Rechargeable Zinc Air Batteries, 45th annual meeting of membrane science of Japan (Research Innovation Center Waseda University), P-31S, November 2023 (in Japanese).
32. Kaito Udo, Mizuki Akatsuka, Masafumi Yamato, Hiroyoshi Kawakami, Temperature dependence of polymer composite membranes containing surface modified nanoparticles with high CO2 permeability, 45th annual meeting of membrane science in Japan & Membrane Symposium 2023, P-15A, Nov. 2023.
33. Natsuki Inoue, Manabu Tanaka, Hiroyoshi Kawakami, Effects of polymer nanofibers on chemical stability of nanofiber composite electrolyte membranes for fuel cells, 45th Annual Meeting of Membrane Science of Japan and Membrane Symposium 2023 in Japan, (Waseda Univ.), P-32S, November 2023 (in Japanese)
34. Ellie Fujiwara, Hiyori Iitsuka, Haruka Mitome, Masahiro Yoshioka, Kiyoshi Sato, Hiroyoshi Kawakami, Induction of Cellular Senescence in Cancer Cells by Epigenetic Control Carriers and Modification of Their Extracellular Vesicles, 45th Annual Meeting of Membrane Science of Japan and Membrane Symposium 2023 in Japan (Waseda Univ.), P-66S, November 2023 (in Japanese)
35. Ryota Inahara, Natsuki Inoue, Kota Iwasaki, Akari Tatsukawa, Manabu Tanaka, Masafumi Yamato, Hiroyoshi Kawakami, Fabrication and fuel cell evaluation of composite electrolyte membranes composed of acid-doped nanofibers for higher proton conductivity over a wide temperature and humidity range, The 64th Battery Symposium in Japan (Osaka International Convention Center), 2H14 , November 2023 (in Japanese)
36. Kenta Sando, Manabu Tanaka, Hiroyoshi Kawakami, Secondary battery evaluation of polymer nanofiber composite electrolyte membranes with different lithium salt concentrations, The 64th Battery Symposium in Japan (Osaka International Convention Center), 2A03, November 2023 (in Japanese)
37. Dong Yubing, Manabu Tanaka, Hiroyoshi Kawakami, Fabrication and Lithium Battery Application of Network-structured Polymer Gel Electrolyte Membranes Containing Solvate Ionic Liquid, The 64th Battery Symposium in Japan (Osaka International Convention Center), 2A02, November 2023 (in Japanese)
38. Hiyori Iitsuka, Haruka Mitome, Masayoshi Yoshioka, Kiyoshi Sato, Hiroyoshi Kawakami, Senescence-induction in cancer cells by epigenetics-controlled carrier and anti-tumor exosome production, The 45th annual meeting of Japanese society of biomaterials (Kobe), November 2023 (in Japanese)
39. Bunta Mizoguchi, Yusuke Fujita, Koki Mino, Masahiro Yoshioka, Kiyoshi Sato, Hiroyoshi Kawakami, Enhanced therapeutic efficacy of activated MSC by mitophagy reactivation, The 45th Annual Meeting of Japanese Society for Biomaterials(Kobe), November 2023
40. Yusuke Fujita, Masahiro Yoshioka, Kiyoshi Sato, Hiroyoshi Kawakami, Production of designer stem cells by administering functional nanocarriers, The 61st Annual Meeting of the Japanese Society Artificial Organs (Tokyo), November 2023.
41. Yosuke Saito, Shun Nakazawa, Kenta Sando, Manabu Tanaka, Hiroyoshi Kawakami, Effects of Nanofiber Composite to Solid Polymer Electrolyte Membranes for Lithium-Ion Batteries, 31th Japan Polyimides & Aromatic Polymers Conference (Tokyo Institute of Technology), P23, November 2023
42. Hiroki Mizuta, Kota Iwasaki, Kazuto Suzuki, Motoki Nishizawa, Manabu Tanaka, Hiroyoshi Kawakami, Fabrication and Fuel Cell Evaluation of Composite Electrolyte Membranes Based on Sulfonated Polyimide Blend Nanofibers, 31th Japan Polyimides & Aromatic Polymers Conference (Tokyo Institute of Technology), P24, November 2023
43. Yuki Shinada, Masafumi Yamato, Magnetic alignment of Layered Double Hydroxides P-18, The Magneto-Science Society of Japan 17th annual convention (Fukui University of Technology), Nov. 2023 (in Japanese).
44. Hiyori Iitsuka, Haruka Mitome, Masahiro Yoshioka, Kiyoshi Sato, Hiroyoshi Kawakami, “Antitumor effects of extracellular vesicles secreted from senescence-induced cancer cells”, The 46th Annual Meeting of the Molecular Biology Society of Japan, December 2023 (Kobe Port Island) (in Japanese).
45. Hanae Nakamura, Masahiro Yoshioka, Yuichi Kinoshita, Momoka Chatani, Akiko Takenouchi, Katsuhiko Yoshizawa, “Inhibitory effects of black soybean seed coat extract (Chrono-Care®) supplementation on breast cancer model in rats”, The 20th Annual Meeting of Society for Functional Food Research (Yonago convention center), Y-1, January, 2024 (in Japanese)
46. Kiyoshi Sato, Yusuke Fujita, Masahiro Yoshioka, Hiroyoshi Kawakami, “Designer stem cells with enhanced therapeutic efficacy by improving mitochondrial quality control mechanisms”, The 23rd Congress of the Japanese Society for Regenerative Medicine, March 2024 (TOKI MESSE Niigata Convention Center) (in Japanese).
47. Masafumi Yamato, Hiroyoshi Kawakami,Thermal Properties of PIM-1 Membranes, The 13th International Congress on Membranes and Membrane Processes(ICOM2023) (Makuhari),July 2023
48. Masafumi Yamato, Hiroyoshi Kawakami, Ultra-gas permeable mixed matrix membrane composed of polymer of intrinsic microporosity (PIM-1) and surface-modified silica nanoparticles, The 13th International Congress on Membranes and Membrane Processes(ICOM2023) (Makuhari),July 2023
49. Masafumi Yamato, Hiroyoshi Kawakami, Development of Surface-Modified Nanoparticle/PIM-1 Composite Membranes Targeting Membrane-based DAC, Sep. 2023 (Takamatsu) (in Japanese)
50. Masafumi Yamato, Hiroyoshi Kawakami, Structure and

Physical Properties of Highly loaded membranes with Silica Nanoparticles, 72nd Symposium on Macromolecules, Sep. 2023 (Takamatsu) (in Japanese)

51. Masafumi Yamato, Yuki Shinada, Magnetic Alignment of Layered Double Hydroxide, 71st JSAP Spring Meeting, Mar. 2024 (Tokyo) (in Japanese)

■Patents

1. Nanofiber adduct, electrolyte membrane, composite electrolyte membrane, fuel cell, Hiroyoshi Kawakami, Kiyoshi Sato, Patent application 2023-91800 (2022/6/2)
2. Complex for eliminating dysfunctional mitochondria and complex for suppressing cellular aging, Hiroyoshi Kawakami, Kiyoshi Sato, Patent No. 7429035 (2024/1/30)
3. Gas Separation Membrane, Hiroyoshi Kawakami, Masafumi Yamato, Takumu Morita, Mizuki Akatsuka, PCT/JP2024/002225 (2024/1/25)

■Awards

1. The 72th SPSI Annual Meeting, Poster Award, Natsuki Inoue, “Chemical durability evaluation of nanofiber composite membranes for polymer electrolyte fuel cells”.
2. he 52nd symposium on medical polymers, Student Presentation Award, Hiyori Iitsuka, “Characterization of cancer senescent cells epigenetically modified by functional nanocarriers”.
3. SCEJ 54th Autumn Meeting, Student Award, Kota Nagano, “Pressure dependence of gas permeation of surface-modified nanoparticle/PIM-1 composite membranes”
4. 45th annual meeting of membrane science in Japan & Membrane Symposium 2023, Student Award, Kaito Udo, “Temperature dependence of polymer composite membranes containing surface modified nanoparticles with high CO2 permeability”.
5. 45th Annual Meeting of Membrane Science of Japan and Membrane Symposium 2023 in Japan, Student Award, Natsuki Inoue, “Effects of polymer nanofibers on chemical stability of nanofiber composite electrolyte membranes for fuel cells”.
6. The 45th Annual Meeting of Japanese Society for Biomaterials, Highlight Presentation, Bunta Mizoguchi, ”Enhanced therapeutic efficacy of activated MSC by mitophagy reactivation”.
7. The Magneto-Science Society of Japan 17th annual convention, Student Poster Award, Yuki Shinada, “Magnetic alignment of Layered Double Hydroxides”.
8. 31th Japan Polyimides & Aromatic Polymers Conference, Student Poster Award, Hiroki Mizuta, Fabrication and Fuel Cell Evaluation of Composite Electrolyte Membranes Based on Sulfonated Polyimide Blend Nanofibers”.

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Doctor's course -1
Master's course -7
Bachelor 4 -4

■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).

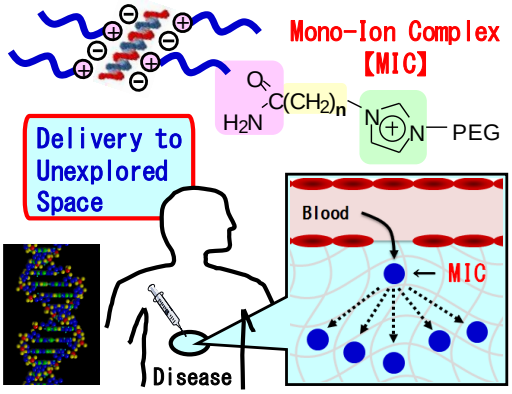

Figure 1. Delivery to *in vivo* unexplored space by the mono-ion complex (MIC).

In this year, we have focused on zwitterionic polymers as an alternative material to PEG and used them as carriers instead of surface modification to form PICs with pDNA, which has a near neutral surface charge and excellent pharmacokinetics in the body. As a result, we enhanced the effect of shRNA in vivo and showed a specific RNA interference effect on Mstn. We found that the zwitterionic polymer/pDNA PIC with high tissue diffusivity in skeletal muscle and inhibition of target gene expression in situ is effective for nucleic acid-based gene therapy.

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).

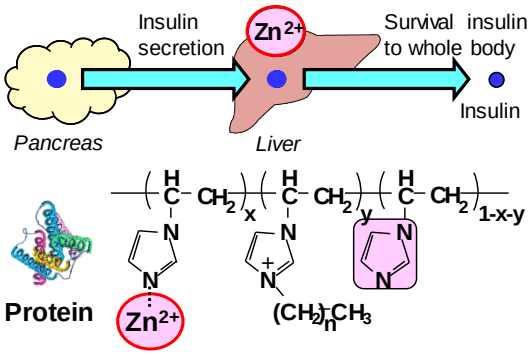

Figure 2. Remote control of hypoglycemic hormone in blood.

In this year, we have prepared Zn^{2+}-encapsulated Chol-Lacto vesicles with targeting ability to hepatic parenchymal cells and prepared carriers for stable and specific delivery of Zn^{2+} to hepatic parenchymal cells. The resulting Zn^{2+}-encapsulated vesicles showed higher intracellular uptake of Zn^{2+} than Zn^{2+} alone. When we used the control cells without ASGP-R, furthermore, the vesicles did not show the higher intracellular uptake. Thus, it is proved that Chol-Lacto vesicles are useful as Zn^{2+} delivery carriers.

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).

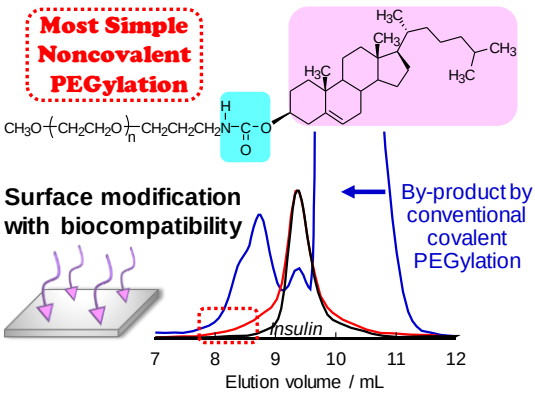

Figure 3. Development of novel bio-function by Chol-PEG.

In this year, the maximum number of modifications per unit surface area to PP surfaces at each coating concentration of Chol-PEG was calculated from the QCM experiments. As a result, more were estimated for PP surfaces coated with the shorter Chol-PEG500 compared to Chol-PEG2000, which has a longer PEG molecular weight. Compared to Chol-PEG2000, the PP surface coated with Chol-PEG500 almost completely inhibited the adsorption of BSA. Thus, the superiority of the modification density of PEG500 over PP surfaces in inhibiting protein adsorption was revealed.

■Papers with Peer Review

1. Ryoto Kon and Shoichiro Asayama, Synthesis of guanidinium-dendrimer-type pDNA carriers for gene delivery into floating blood cells, *Polymers for Advanced Technologies*, 34, 3289-3295 (2023).
2. Ren Misaizu and Shoichiro Asayama, Synthesis of N-oxide poly(1-vinylimidazole) for pDNA delivery systems *in vivo*, *Chemistry Letters*, accepted.

■Reviews

See the annual report in Japanese (2 articles).

■Academic Meeting

See the annual report in Japanese (15 articles).

■Patents

See the annual report in Japanese (1 patent).

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Doctor's course -2
Master's course -7
Bachelor -6

■**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. As a successful example, the fabrication of lactam-ring-containing rhodamine-grafted boronate particles enabled us to detect change in afterglow by adding Al3+, as a result of Förster-type energy transfer from the phosphorescent **BP** to the Al^{3+}-interacting rhodamine dye **1** on the surface (Figure 1). Furthermore, quantitative structure-property relationship (QSPR) analysis between the nanostructure and RTP behavior of boronate assemblies was elucidated by chemometrics methodology (Figure 2).

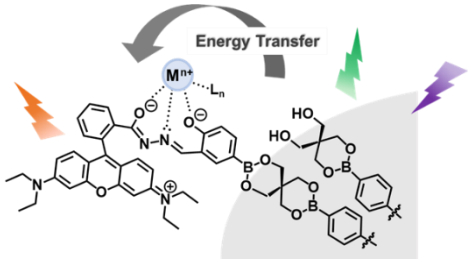

Figure 1. Metal ion-responsive afterglow martials.

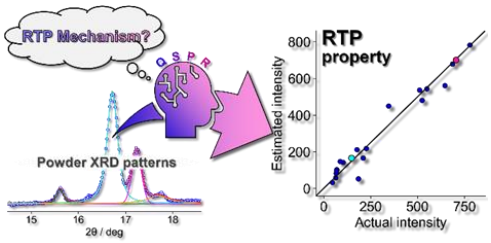

Figure 2. Chemometrics-assisted QSPR analysis.

2. Turn-on type afterglow probe for Hg^{2+} sensing by a PVA-mediated triplet sensitizer

Yuji Kubo

Abstract

Chemical stimulus afterglow systems have attracted much attention because of their potential applications in time-gated bioimaging and background-free chemosensors. However, this development is at the frontier because introducing a chemical-stimulus acceptable site may facilitate a competitive deactivation process by molecular vibration and oxygen, making it difficult to stabilize the triplet state. Therefore, it remains challenging to develop chemosensing in the afterglow. In this study, benzophenone-containing boronate crosslinked poly(vinyl alcohol) (PVA) (**BPB@PVA**) was prepared for the first time to investigate whether the resultant PVA served as a triplet sensitizer. We found that 9H-thioxanthene-2-methoxy-9-thione **1** was doped into **BPB@PVA** film, and the resultant film **1/BPB@PVA** (1:20:1000) displayed Hg^{2+}-induced afterglow response with a lifetime of 75.9 ms, accompanying with yellowish green emission after ceasing irradiation light at 254 nm. The desulfurization of **1** by Hg^{2+} in the PVA film produces room-temperature phosphorescence (RTP)-active thioxanthene-2-methoxy-9-one **2**, the emission quantum yield being increased by benzophenone-derived cross linkage (Figure 3).

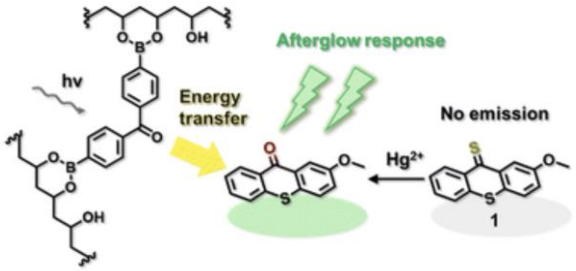

Figure 3. Turn-on type afterglow material using benzophenone-containing bronate crosslinked PVA.

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3. Thermochromic afterglow from benzene-1,4-dibronic acid-doped co-crystals

Yuji Kubo

Abstract

The accurate thermosensing requires a minimum impact of autofluorescence and light scattering from the samples. In this study, we discovered that commercially available benzene-1,4-diboronic acid (**BDBA**) doped co-crystals with trimethylolpropane (**TMP**) exhibit excellent thermochromic dual phosphorescence properties over a wide temperature range from –132 to 40°C, despite its simple structure that does not have any donor-acceptor linkage. The dual phosphorescence was consisted of monomeric benzene-1,4-diboronate (**BDBA** ester) and aggregation-stabilized species (Figure 4).

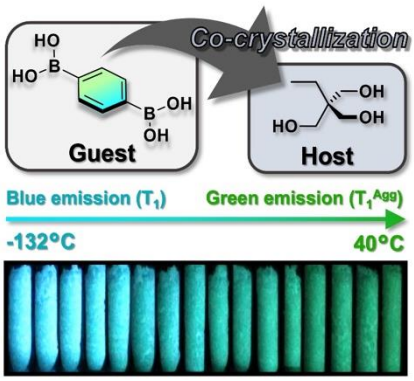

Figure 4. Thermochromic afterglow using a co-crystal approach.

4. 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 (ε = 1.07×10^5 M^{-1} cm^{-1}) in THF. In the presentation, the photocatalytic activity of **1**-loaded TiO_2 is discussed.

6. Evaluation of the effect of peripheral aryl groups on the physical properties of electron-rich heteroacenes

Masato Ito

Abstract

Near-infrared luminescent materials are expected to be applied to super-resolution biological imaging and information technology. In this study, we focused on electron-rich heteroacenes containing oxygen atoms in the acene skeleton and synthesized derivatives with various substituents at appropriate positions to achieve luminescence in the long-wavelength region. We also clarified the effect of peripheral Aryl groups on not only the photophysical properties but also diradical properties by expanding central π-conjugated skeleton (Figure 5).

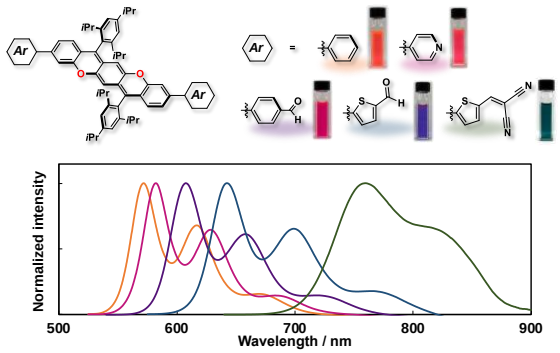

Figure 5. Molecular design of oxygen-containing heteroacenes and their emission properties.

■Papers with Peer Review

1. M. Kawashiro, T. Mori, M. Ito, N. Ando and S. Shigehiro, Photodissociative modules that control dual-emission properties in donor–π–acceptor organoborane fluorophores, *Angew. Chem. Int. Ed.*, **2023**, 62, e20303725. DOI: 10.1002/anie.202303725

2. S. Takegawa, M. Ito and Y. Kubo, Turn-on type afterglow probe for Hg^{2+} sensing by a PVA-mediated triplet sensitizer, *New. J. Chem.*, **2023**, 47, 12554–12560. DOI: 10.1039/D3NJ01281F

3. R. Hasegawa, M. Ito, and Y. Kubo, Tuning the triplet population of arylselanyl-BODIPY photosensitizers through substituents engineering for triplet-triplet annihilation photon upconversion with perylene, *J. Porphyr, Phthalocyanines*, 2023, 27, 757–764. DOI: 10.1142/S1088424623500037

4. K. Kawaguchi, N. Sugawara, M. Ito and Y. Kubo, Thermochromic afterglow from benzene 1,4-diboronic acid-doped co-crystals, *Chem. Eur. J.*, **2024**, e202303924. DOI: 10.1002/chem.202303924

■Books

See the annual report in Japanese 1 book (Y. Kubo wrote his separate part.)

■Academic Meeting

＊Domestic

See the annual report in Japanese (17 articles)

■Awards

See the annual report in Japanese.

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Doctor's course -1
Master's course -8
Bachelor 5

■**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. Artificial Molecular Rotors

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.

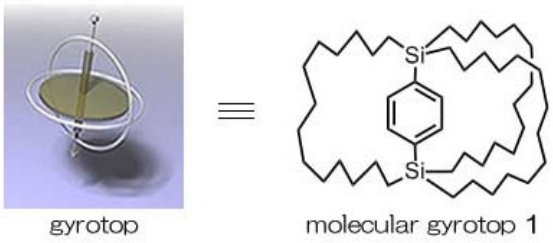

Figure 1. molecular gyrotop.

The fluorescence of organic molecules has been extensively studied for the development of functional materials. Clarifying the relationship between molecular motion and fluorescence quantum yield (FQY) can aid in developing intensity-controllable fluorophores. This study compared the FQYs of 9,9-dimethylfluorene-diyl bridged disilabicyclo[n.n.n]alkanes in solution and solid state. Two macrocage derivatives, C18 (n = 18) and C22 (n = 22), were synthesized, and their structures were characterized. The FQYs in solution were almost the same, but the FQY in the solid state of large-cage C22 was smaller than that of small-cage C18. The lower FQY of C22 was attributed to the librational motion, which occurs on a time scale close to the fluorescence time scale. The solid-state 2H NMR showed that the slight motion of the deuterated fluorophore, such as libration, inside the cage causes more efficient relaxation. The results of this study are expected to contribute to the molecular design of environmentally responsive fluorescent materials (Figure 2, article #3).

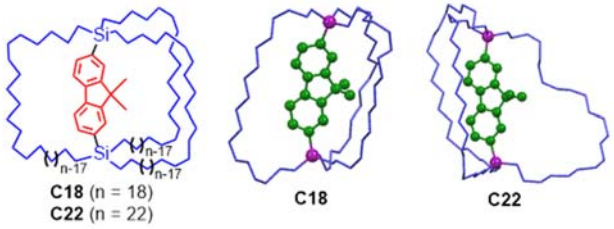

Figure 2. Fluorene-diyl bridged molecular gyrotops (article #3).

Phenylenediamine derivatives with oxidation properties, specifically phenylene-bridged diazacycloalkanes of varying chain lengths (C10, C12, and C14) were investigated. X-ray crystallography revealed differences in the structures around nitrogen atoms depending on chain length, with C10 having a perpendicular benzene plane and C14 having a co-planar plane

2. Disilabicycloalkanes

In large bicycloalkanes, several in/out forms exist, wherein substituents on the bridgehead atoms are oriented either outside or inside the cage. The relative stability between the in,out and twist-out,out forms, which can interconvert through homeomorphic conversion, was found to depend upon the cage size. The in,out form demonstrated thermodynamic stability in the smaller C10-chains derivative, whereas the twist-out,out form prevailed in the larger derivatives of C14 and C18-chains plausibly as a result of dispersion forces among the chains. (Figure 3, article #1)

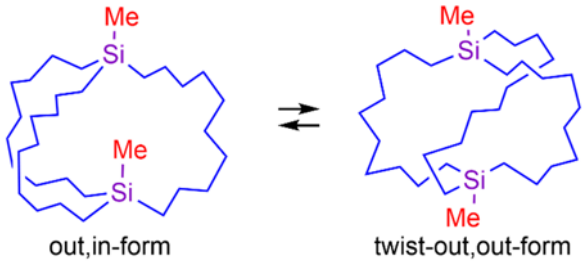

Figure 3. Disilabicycloalkanes (article #1).

Figure 4 displays the front cover of the journal issue that includes the article #1.

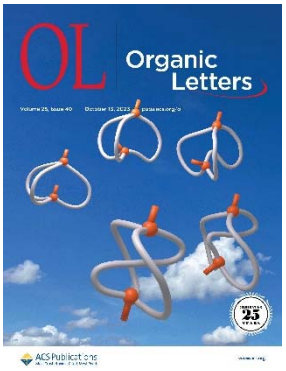

Figure 4. A cover picture of the journal issue including the article #1.

3. Stannane-based Mmolecular Bevel Gears

Ditriptycylmethanes are known as molecular bevel gears because the two triptycyl groups act as wheels and display correlated rotation in solution. However, introduction of substituents on the methylene junction for chemical modification of the bevel gears has been difficult due to steric hindrance of the triptycyls. In this study, stannane-based molecular bevel gears with organic substituents on the tin linker were achieved by utilizing long Sn–C bonds. Ditriptycylstannanes with methyls or phenyls on the tin atoms were synthesized. Their structures were characterized by X-ray crystallography, and the angle of triptycyl– Sn–triptycyl in the diphenyl derivative was observed to be narrower than that of the dimethyl derivative due to steric hindrance of the phenyls. The gear rotation of these derivatives was observed by NMR spectroscopy through observations of the phase isomers of the corresponding methyltriptycyl derivatives. Gear slippage was observed in the high-temperature region, and the activation energy of the diphenyl derivative was higher than that of the dimethyl derivative. The observed relationship between gear rotation and substituents on the tin can aid in the molecular design of functional molecular bevel gears. (Figure 5, article #2).

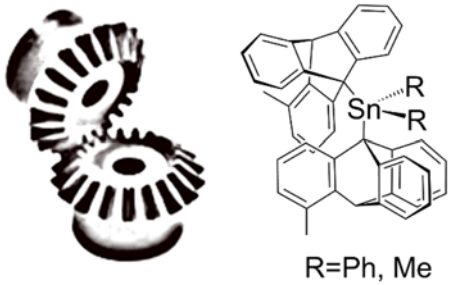

Figure 5. Stannane-based molecular bevel gears (article #2).

■Papers with Peer Review

1. Synthesis of Dimethyldisilabicycloalkanes: Cage-Size Effects on the Relative Stabilities between In,Out and Twist-Out,Out Forms, Wataru Setaka*, Yuto Ikeda, Yusuke Inagaki, Kazuaki Ohara, and Kentaro Yamaguchi, *Org. Lett.* **2023,** 25, 7283–7286. (selected as a Front Cover)
   (DOI: 10.1021/acs.orglett.3c02382)
2. Synthesis and structure of stannane-based molecular bevel gears having substituents on a tin linker, Satoshi Hosono, Yusuke Inagaki and Wataru Setaka*, *Org. Biomol. Chem.* **2023,** 21, 4781–4787.
   (DOI: 10.1039/d3ob00666b)
3. Synthesis and fluorescence properties of 9,9-dimethylfluorene-diyl bridged molecular gyrotops: Effects of slight fluorophore motion on fluorescence efficiency in solid state, R. Yoshizawa, Y. Inagaki, H. Momma, E. Kwon, K. Ohara, K. Yamaguchi, and W. Setaka, *New. J. Chem.* **2023**, *47*, 5946-5952.
   (DOI:10.1039/D2NJ05873A)

■Invited Lectures

1. Wataru Setaka,
   Dielectric Relaxation of Crystalline Molecular Gyrotops with a Dipolar Rotor, 13th International Advances in Applied Physics & Materials Science Congress & Exhibition (APMAS2023), 2023.10.11-17. (Oludeniz, Turkey). (10/13 plenary talk, Invited).

■Academic Meeting

＊Domestic

See the annual report in Japanese (21 articles)

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Doctor's course - 2
Master's course -9
Bachelor 4 -5

■**Outlines of the Research**

1. Studies on inorganic materials and energy devices

Koichi KAJIHARA, Masanao ISHIJIMA

We are studying energy devices using inorganic solids. A new lithium-containing sodalite $Li_8B_6Si_6O_{24}Cl_2$ was discovered. This compound was the first alkali sodalite containing boron as the main framework cations, and the first sodalite that can form glass-ceramics from uniform melts. The resulting glass-ceramics were lithium ion conducting and stable in contact with lithium metal. We also succeeded the synthesis oand single crystal X-ray structure analysis of $Na_4B_4Al_3O_{12}Cl$, which is the first sodium boracite. The resulting structure data contribute to fundamental solid-state sciences.

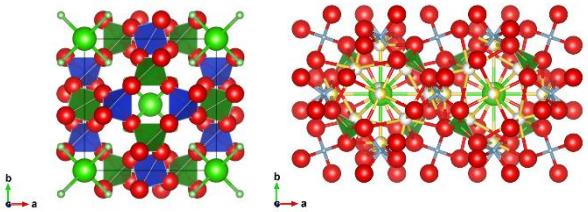

Fig. 1 Crystal structures of $Li_8B_6Si_6O_{24}Cl_2$ (left) and $Na_4B_4Al_3O_{12}Cl$ (right).

Silicon is a ubiquitous element and its utilization is in accordance with SDGs. We found that poly(cyclohexylsilsesuquioxane) synthesized by cosolvent-free method developed in our lab is a glass with low melting temperature. In contrast to the well-known poly(phenylsilsesquioxane) glasses, poly(cyclohexyl-silsesquioxan) glasses and their copolymers with alkylsilsesquioxanes were transparent to deep-UV light with wavelengths equal or less than 300 nm. In addition, they are hydrophilic and strongly bonded to glasses and metals because of the presence of residual SiOH groups. However, the polycondensation between the SiOH groups was slow and the glasses maintained thermoplasticity upon heating to 200°C.

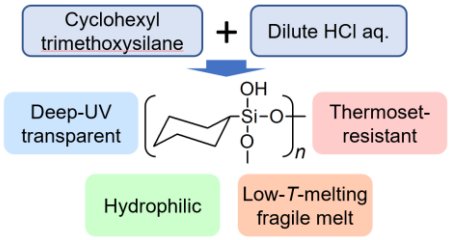

Fig. 2 Cosolvent-free synthesis of hydrophilic thermoset-resistant deep-ultraviolet-transparent poly(cyclohexylsilses-quioxane)-based glasses with low melting temperatures.

Masanao ISHIJIMA

CuPd alloy has two crystal phases, and crystal phase control of nanoparticles was carried out by the annealing process. controlled We developed a method for synthesizing CuPd nanoparticles with different crystal phases by adjusting the reduction rate using complexing agents in the alcohol reduction method and investigated their properties as electrochemical reduction catalysts for CO_2.

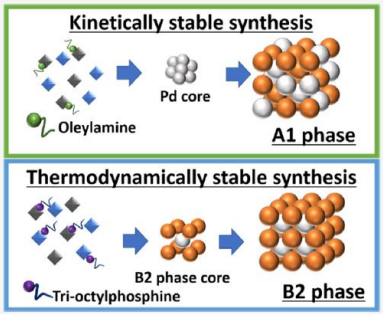

Fig. 3 Crystal phase control of CuPd nanoparticles

■**Papers with Peer Review**

1. H. Arima, N. Tezuka, M. Ishijima, K. Kanamura, K. Kajihara, "Lithium-ion-conducting glass-ceramics of a boron-containing alkali sodalite $Li_8B_6Si_6O_{24}Cl_2$," J. Ceram. Soc. Jpn. **131**, 291-297 (2023)
2. K. Kajihara, R. Suzuki, R. Seto, H. Itakura, M. Ishijima, "Poly(cyclohexylsilsesquioxane)-based hydrophilic thermoset-resistant deep-ultraviolet-transparent glasses with low melting temperatures," ACS Appl. Mater. Interfaces **15**, 31880-31887 (2023).
3. Y. Shimbori, K. Nishikawa, K. Kajihara, K. Kanamura, "Application of 3DOM PI separator to Li metal battery with highly concentrated ionic liquid electrolyte," Electrochemistry **91**, 127003 (2023).
4. N. Todoroki, M. Ishijima, J. L. Cuya Huaman, Y. Tanaka, J. Balachandran, Composition sensitive selectivity and activity of electrochemical carbon dioxide reduction on Pd–Cu solid-solution alloy nanoparticles, Catal. Sci. Technol., **13**, 5025 (2023).
5. M. Ishijima, N. Todoroki, J. L. Cuya Huaman, Y. Tanaka, J. Balachandran, Kinetically Controlled Direct Synthesis of B2- and A1-Structured Cu–Pd Nanoparticles, Inorg. Chem., **62**, 19270 (2023).
6. K. Kajihara, S. Nakagawa, R. Nakagawa, M. Suda, M. Ishijima, H. Kuriyama, I. Serizawa, "Temperature dependence of narrow-band uvb photoluminescence of silica–(Gd,Pr)PO_4 transparent glass-ceramic phosphors," J.

Phys: Condens. Matter **36**, 085301 (2024).

7. S. Yoshino, H. Arima, M. Ishijima, K. Kajihara, "Crystal structures of the alkali aluminoboracites $A_4B_4Al_3O_{12}Cl$ (A = Li, Na)," Acta. Cryst. E **80**, 169-173 (2024).
8. Y. Shimbori, S. Ooga, K. Kajihara, K. Kanamura, "Effect of Polybenzimidazole Addition to Three-Dimensionally Ordered Macroporous Polyimide Separators on Mechanical Properties and Electrochemical Performances", Electrochemistry, DOI: 10.5796/electrochemistry.23-00145.

■Reviews and Books

See the annual report in Japanese (3 articles)

■Invited Lectures

＊International

1. Koichi Kajihara. Synthesis and characterization of lithium-ion-conducting boracite and sodalite glass-ceramics. ICG Annual Meeting 2023. 2023/11, China (Invited)

＊Domestic

See the annual report in Japanese (1 article)

■Academic Meeting

＊International

2. Koichi Kajihara, Shingo Nakagawa, Masanao Ishijima. Temperature dependence of narrow-band UVB photoluminescence of silica–(Gd,Pr)PO_4 transparent glass-ceramics. The 14th International Conference on SiO_2, Dielectrics and Related Devices, 2023/6, Italy
3. Yuma Shimbori, Koichi Kajihara, Kiyoshi Kanamura. Improvement of Charge/Discharge Performance of Li Metal Battery Using Ionic Liquid Electrolyte with 3DOM PI Separator. 224th ECS Meeting. 2023/10, Sweden
4. Masanao Ishijima. Development of the Alcohol Reduction Method for the Designed Synthesis of Bimetallic Nanomaterials. Future Materials 2023. 2023/10, Online

＊Domestic

See the annual report in Japanese (9 articles)

■Patents

See the annual report in Japanese (3 articles)

■Awards

See the annual report in Japanese (3 articles)

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Doctor's course -1
Master's course -5
Bachelor 4 -4

■**Outlines of the Research**

1. Fabrication of Nanofilters by Electrochemical Process
Takashi YANAGISHITA

We have investigated a membrane filter that can efficiently separate fine particles by anodization of Al. Based on the optimization of the geometry, a membrane filter was successfully fabricated that significantly exceeds the solution permeability of usual membranes.

2. Application of anodic porous alumina prepared by anodization of Al
Takashi YANAGISHITA

A wettability gradient surface was formed by continuously changing the surface pore size of porous alumina formed by anodic oxidation of Al. The obtained surface was found to function as a surface that spontaneously transports water droplets. The formation of ultrafine nanofibers with uniform size was also achieved by spinning polymer nanofibers using porous alumina as a mouthpiece.

3. Preparation of ordered nanohole arrays and their applications
Takashi Yanagishita, Hirokazu MUNAKATA

It was found that highly ordered nanohole arrays can be formed by anodic oxidation of various metals, including stainless steel. The application of the obtained highly ordered nanohole arrays to electrolytic capacitors was also investigated.

4. Research on fuel cells
Hirokazu MUNAKATA, Takashi YANAGISHITA

Elevating the operating temperature of fuel cells is crucial for enhancing the activity of fuel catalysts and mitigating their poisoning with carbon monoxide. Toward achieving this goal, we have synthesized and evaluated OH^- conductive ionic liquids with high thermal stability and ion conductivity as intermediate temperature fuel cell electrolytes. The progress of oxygen reduction reaction (ORR) was successfully confirmed in those ionic liquids at temperatures above 100 °C under non-humid conditions. However, the overpotential for ORR was high due to the adsorption of ionic species on platinum catalytsts. To solve this issue, the electronic state of platinum catalysts was tried to control by using heteroatom-doped graphene derivatives as the catalyst supports, and found that those with electron donating properies are suitable to reduce the overpotential for ORR in OH- conducting ionic liquids.

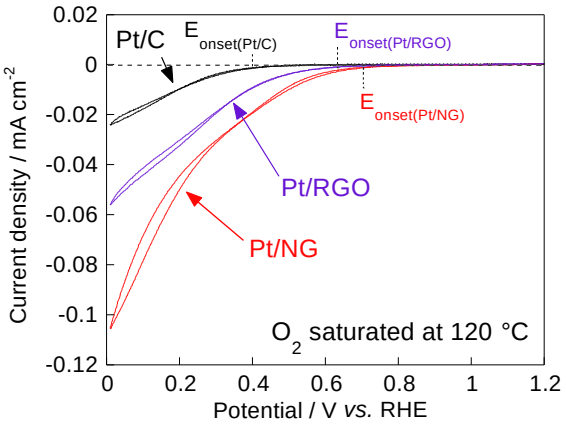

Fig. 1 Electrochemcial oxygen reduction reaction of platinum catalysts suppoterd on Ketjen Black (Pt/C), reduced graphene oxide (Pt/RGO) and nitrogen-doped graphene (Pt/NG) in OH^- conducting ionic liquid.

■Papers with Peer Review

1. Preparation of alumina membrane filters with framework structures by Al anodization
   Y. Boushi and T. Yanagishita*, Langmuir, in press.
   [Supplementary Cover Art]
2. Control of water droplet transport using anodic porous alumina with wettability gradient
   Y. Boushi and T. Yanagishita*, Langmuir, in press.
   [Supplementary Cover Art]
3. Anodic Porous Alumina Membranes with Chemical Stability Improved by Atomic Layer Deposition Coating of TiO_2
   H. Itoh and T. Yanagishita*, ECS J. Solid State Sci. Technol., 13, 023002 (2024).
4. Preparation of ordered nanostructures by anodization of Ag substrate with depression patterns
   S. Teshima and T. Yanagishita*, J. Electrochem. Soc., 170, 123503 (2023).
5. Flat and roll-type translucent anodic porous alumina molds anodized in oxalic acid for UV nanoimprint lithography
   T. Yanagishita*, N. Kumagai, and H. Masuda, RSC Adv., 13, 33231 (2023).
6. Anisotropic Plasmonic Property of Al Nanowires Obtained by AC Electrodeposition Using Anodic Porous Alumina Template
   T. Kondo*, T. Sano, T. Yanagishita, and H. Masuda, J. Phys. Chem. C, 127, 21629 (2023). **[Supplementary Cover Art]**
7. Fabrication of nanoparticle assemblies with a controlled number of constituent nanoparticles by membrane emulsification using anodic porous alumina
   T. Yanagishita*, K. Yuda, T. Kondo, and H. Masuda, Mater. Adv., 4, 4369 (2023). **[Inside Front Cover]**
8. Effects of anodization conditions of stainless steel on the formation of ordered nanoporous structures with high aspect ratios
   Y. Osada and T. Yanagishita*, Nanotechnology, 34, 465601 (2023).
9. Investigation of conditions for preparation of ordered nanohole arrays by anodization of iron substrates with depression patterns
   Y. Osada and T. Yanagishita*, J. Electrochem. Soc., 170, 063510 (2023).
10. Preparation of antireflection structures with heat resistance by nanoimprinting using anodic porous alumina molds
    T. Yanagishita*, R. Ooe, Y. Ishibashi, and T. Mitsuru, Jpn. J. Appl. Phys., 62, 068002 (2023).
11. Preparation of Size-controlled LiCoPO4 Particles by Membrane Emulsification Using Anodic Porous Alumina and Their Application as Cathode Active Materials for Li-ion Secondary Batteries
    T. Yanagishita*, R. Otomo, and H. Masuda, RSC Adv., 13, 16549 (2023).
12. Fabrication of moth-eye structures with precisely controlled shapes by nanoimprinting using anodic porous alumina molds
    T. Yanagishita*, M. Etani, and T. Kondo, J. Electrochem. Soc., 170, 063501 (2023).
13. Preparation of polymer nanopillar arrays with controlled tip shapes and their application to hydrophobic and oleophobic surfaces
    T. Yanagishita*, M. Kurita, Langmuir, 39, 8540 (2023).
    [Supplementary Cover Art]
14. Fabrication of Ideally Ordered Anodic Porous Alumina on Glass Substrates by Stamping Process Using Flexible Stamps
    K. Kato and T. Yanagishita*, ECS Adv.,2, 022501 (2023).
15. J. Song, S.-H. Lim, K.-G. Kim, N. Umirov, H. Lee, C.B. Dzakpasu, J. Lim, J. Nam, J. Park, J.-N. Lee, H. Munakata, K. Kanamura, S.-S. Kim, Y.M. Lee, Adv. Energy Mater., 13 2004328 (2023).
16. M.U. Salma, Y. Maruyama, M. Nagao, S. Watauchi, H. Munakata, K. Kanamura, I. Tanaka, J. Ceram. Soc. Jpn., 131, 72 (2023).
17. M.R. Khandaker, Y. Maruyama, M. Nagao, S. Watauchi, H. Munakata, K. Kanamura, I. Tanaka, Cryst. Growth Des., 23, 5699 (2023).
18. Ji.S. Yun, O. Mukhan, W. Cho, J.-. Yu, H. Munakata, K. Kanamura, S.-S. Kim, Adv. Sustainable Syst. 2300297, (2023).
19. O. Mukhan, J.-S Yun, H. Munakata, K. Kanamura, S.-S. Kim, ACS Omega 2024, 9, 4004 (2024).

■Invited Lectures

＊International

1. H. Munakata, R. Wakabayashi, K. Kanamura
   Development of hydroxide ion conducting ionic liquids for non-humidified intermediate temperature alkaline-type fuel cells,
   International Conference on Nanomaterials and Energy Storage Systems (INESS-2023), 2023 年 7 月, Akyaka, Turkey
2. T. Yanagishita and Y. Boushi
   Fabrication of anodic porous alumina with wettability gradient
   ICSE 2023, 2023 年 11 月, Korea.

＊Domestic

See the annual report in Japanese (4 articles)

■Academic Meeting

See the annual report in Japanese (33 articles)

■Patents

See the annual report in Japanese (3 articles)

■Awards

See the annual report in Japanese (3 articles)

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Visiting researcher 3
Doctor's course 3
Master's course 13
Bachelor 6

■**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.

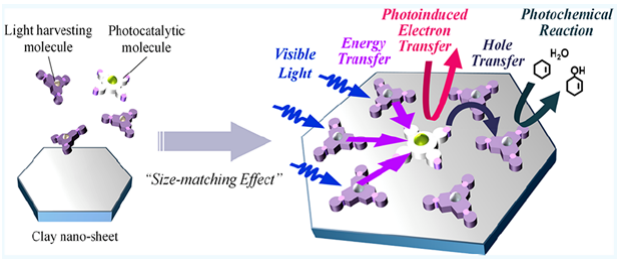


Fig. 1. Artificial light harvesting model on the nanosheet.

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.

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.

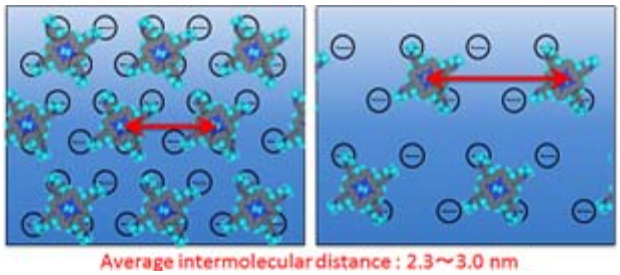


Fig. 2. An example of our methodology to control the adsorption structure of dyes on the clay surface by using a suitable clay species.

3. Research on protein behavior on inorganic nanosheets

Shinsuke TAKAGI, Tetsuya SHIMADA

Proteins take unique higher-order structures and exhibit unique properties in an aquatic environment. For example, enzymes have extremely high substrate selectivity based on their higher order structure. Horseradish peroxidase (HRP) is known to selectively react with hydrogen peroxide. It was found that when this HRP was adsorbed onto clay nanosheets, its structure changed and the enzymatic activity changed. It becomes possible to react with sterically bulky peroxides that cannot react in water. It was also found that the heat resistance of HRP was greatly improved on nanosheets.

4. Surface-induced emission (S-FIE) on the clay surface

Shinsuke TAKAGI, Tetsuya SHIMADA

Usually, dyes have their emission intensity determined by the characteristics based on their molecular structure. On the other hand, in this study, we found that even dyes with extremely weak emission can often enhance emission by being adsorbed on

nanosheets in a non-associated state. Depending on the dye, emission enhancement of more than 100 times was observed, and it is a useful technique for the development of optical functional materials. This year, we found that emission enhancement can be achieved not only with fluorescence but also with phosphorescence.

Videos can be viewed on the following site.
https://www.apchem.ues.tmu.ac.jp/labs/takagi/S_FIEss.mp4

Fig. 3. Enhancement of emission by addition of nanosheets.

5. Research on preparation of semiconductor nanosheet-dye complex

Shinsuke TAKAGI, Tetsuya SHIMADA

Since clay minerals are insulators, they themselves do not have redoxactivity. Therefore, we designed and synthesized new semiconductor nanosheets, and examined their complex formation behavior with dyes. As a result, it was clarified that, like clay mineral nanosheets, it is possible to realize a high-density, non-associated adsorption structure for dyes. As a result, new knowledge was obtained for the construction of solar cells and artificial photosynthetic systems.

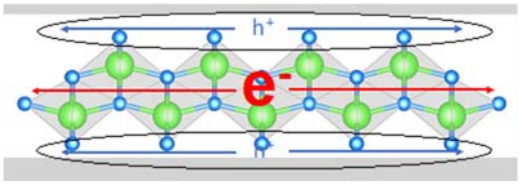


Fig. 4. Visible-light hydrogen generation reaction using the anisotropy of semiconductor nanosheets.

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.

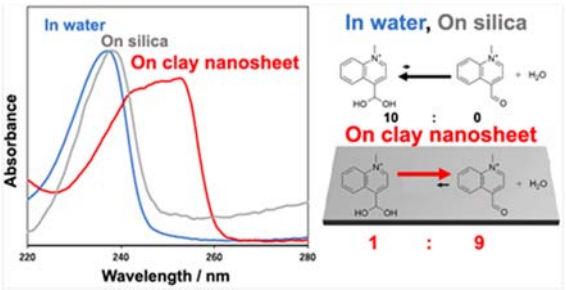


Fig. 5. The equilibrium between aldehyde (MQu^+-Aldehyde) and diol (MQu^+-Diol) in water without and with clay nanosheet.

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.

7. Research on supported gold catalysts

Tamao ISHIDA

Au nanoparticles with a diameter of 5 nm or less are known to show high catalytic activity for CO oxidation when supported on reducible metal oxides such as Co_3O_4 and NiO. For CO oxidation, the interface between Au and the supports is regarded as the active site, and molecular oxygen is activated at the oxygen vacancies of the oxide supports near the interface. Therefore, it is important to deposit Au particles as small as possible on oxides having abundant oxygen vacancies in order to exhibit high activity.

Layered double hydroxides (LDHs) are compounds in which layered divalent metal hydroxide is partly replaced by trivalent metal ions, and LDH composed of various metals can be prepared. LDHs can be converted into mixed metal oxides (MMOs) by air calcination. It has been reported that when nanometer-sized Ni-Ti LDHs are converted to MMOs, NiO and TiO2 domains in MMOs possess abundant Ni defects (Ni^{3+}) and oxygen vacancies (Ti^{3+}), respectively. Therefore, small Ni-Ti MMO derived from LDH can be expected to be a suitable support for highly active Au catalysts.

In this study, we deposited ultrafine Ni-Ti LDH on SiO_2 and immobilized Au clusters of less than 2 nm in a diameter (Figure 6a) by various preparation methods: LDH on SiO_2 was converted to MMO and then Au was deposited on MMO/SiO_2 by deposition-precipitation (DP) or DP with urea (MMO-DP, MMO-DPU), and Au was deposited on LDH by DP or DPU followed by transformation into MMO (LDH-DP, LDH-DPU). The catalytic activity was evaluated by CO oxidation. LDH-DPU exhibited the highest catalytic activity (Figure 6b). X-ray photoelectron spectroscopy revealed that the amounts of Ni^{3+} and Ti^{3+} varied depending on the preparation method and that the amount of Ti^{3+} contributed to the catalytic activity. Given that the amount of Ti^{3+} is reflected the amount of oxygen vacancies where O_2 is activated, LDH-DPU having rich oxygen vacancies exhibited the higest catalytic activity.

The LDH-DPU (Au/Ni-Ti MMO/SiO_2), which exhibited the highest catalytic activity, showed a 50% CO conversion temperature ($T_{1/2}$) down to 10 °C. This value is the lowest amoung Au on bulk Ni-Ti MMO ($T_{1/2}$ 24 °C) and conventional Au catalysts such as Au/TiO_2 and Au/NiO (Figure 6b). To evaluate the O_2 activation, temperature-programmed reaction of CO (CO-TPR) was conducted. The catalyst was pretreated with O_2 and then heated under CO flow to monitor the amount of CO_2 produced. LDH-DPU showed CO_2 production from around −40 °C, while other catalysts showed the peak higher than room temperature. The results suggest that O_2 adsorbed on the oxygen vacancies or the lattice oxygen of TiO_2 domain more easily reacted with CO to form CO_2 at lower temperature than those of other catalysts such as LDH-DP, MMO-DP, and MMO-DPU.

The catalytic activity of Au is known to strongly depend on on the type of supports, and the same trend is observed for organic reactions. The transformation of CO_2 to valuable compounds is important in a view of carbon-neutral strategy and has been intensively studied. In this study, *N*-formylation of amines with CO_2 and H_2 was investigated over various kinds of oxide-supported Au catalysts. It has been reported that Au/TiO_2 is highly catalytically active for the *N*-formylation reaction, while other basic, amphoteric, and acidic oxide-supported Au catalysts are completely inactive.

However, it was found in this study that *N*-formylation reaction proceeds by various Au catalysts (Table 1). Among them, Au on deformed orthorhombic Nb_2O_5 (Au/Nb_2O_5-DO) exhibited higher activity (entry 8) than the previously reported Au/TiO_2 (entry 5). For CO_2 hydrogention, methyl formate was

obtained as the major product when amphoteric TiO_2 and acidic Nb_2O_5 were used as supports, while other oxide supported Au catalysts gave methanol as the major product. From this result, the high activity for *N*-formylation was ascribed to the high methyl formate selectivity. Furthermore, Au/Nb_2O_5-DO showed higher activity than Au on amorphous Nb_2O_5-A (Au/Nb_2O_5-A) and on orthorhombic Nb_2O_5-T (Au/Nb_2O_5-T). Given that Au/Nb_2O_5-DO possesses higher acid and base sites than Nb_2O_5-A and –T, the higher acid and base contents would affect the catalytic activity.

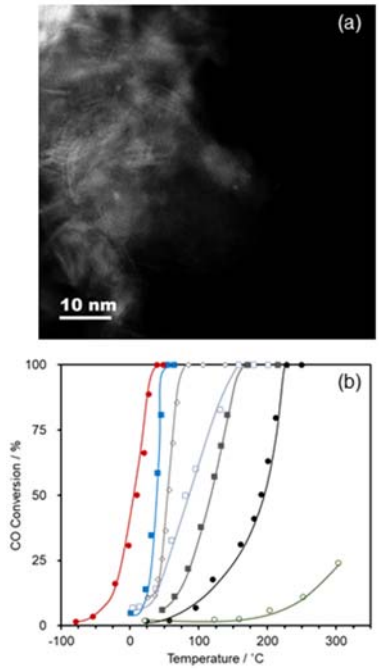
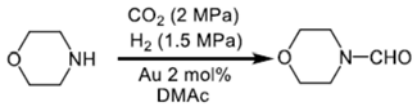


Fig. 6. HAADF-STEM image of LDH-DPU (Au/Ni-Ti MMO/SiO_2) (a) and conversion curves for CO oxidation (b). (b) ■: LDH-DP, ●: LDH-DPU, ■: MMO-DP, ●: MMO-DPU, ◊: Au/TiO_2, □: Au/NiO, ○: Au/SiO_2. Reaction conditions: 0.1 g of catalyst, 1 vol% CO in air (33.3 mL min^{-1}), and space velocity (SV) of 20,000 mL h^{-1} g_{cat}^{-1}.

Table 1. *N*-formylation of morpholine using CO_2 and H_2 over supported Au catalysts.[a]



Entry	Catalyst	Au size /nm[b]	Temp. /°C	Yield /%[c]	HCO_2Me Selec./%[d]
1	Au/ZnO	2.0±0.7	120	4	9
2	Au/CeO_2	4.5±2.7	120	8	–
3	Au/ZrO_2	3.3±1.8	120	11	11
4	Au/Al_2O_3	3.5±2.4	120	24	29
5	Au/TiO_2	4.1±2.2	120	59	66
6			100	55	–
7	Au/Nb_2O_5-DO	2.8±0.7	120	69	–
8			100	80	96
9	Au/Nb_2O_5-T	2.8±0.7	100	48	–
10	Au/Nb_2O_5-A	2.6±0.6	100	24	–

[a] Reaction conditions: morpholine (0.5 mmol), *N*,*N*-dimethylacetamide (DMAc) (3.0 mL), 1 wt% Au catalyst (197 mg, Au 2 mol%), CO_2 (2.0 MPa), H_2 (1.5 MPa), 5 h. [b] Estimated by HAADF-STEM. [c] Yield was calculated by gas chromatography using 1,2-dimethoxyethane as an internal standard. [d] Reaction conditions for CO_2 hydrogenation: DMAc (3.0 mL), 1 wt% Au catalyst (197 mg), CO_2 (1.5 MPa), H_2 (2.0 MPa), 5 h. The selectivity to methyl formate was calculated by the amount of methyl formate produced divided by the total amount of methyl formate and methanol produced.

■Papers with Peer Review

1. Photo-Cyclization, Photo-Ring Opening and Thermo-Ring Opening Reaction of Cationic Diarylethene Adsorbed on the Clay Nanosheet Surface, K. Arakawa, T. Shimada, T. Ishida, S. Takagi, *Colloid. Surf. A Physicochem. Eng. Asp.* **657**, 130537-130543 (2023) . DOI:10.1016/j.colsurfa.2022.130537
2. Enhanced Fluorescence Behavior of Safranine-O by Complexing with Inorganic Clay Nanosheets, M. R. Melechalil, K. Arakawa, Y. Hirade, F. Kuttassery, T. Shimada, T. Ishida, S. Takagi, *J. Photoch. Photobio.* **15**, 100182-100188 (2023) . DOI:10.1016/j.jpap.2023.100182
3. Anionic Clay Surface Facilitates Electron Transfer between an Excited Donor Encapsulated within a Cationic Capsule and a Cationic Electron Acceptor, N. Morita, A. Raj, T. Fujimura, T. Shimada, V. Ramamurthy, S. Takagi, *J. Photoch. Photobio.* **17**, 100204-100208 (2023) . DOI:10.1016/j.jpap.2023.100204
4. Effect of Poly (*N*-Vinylpyrrolidone) Ligand on Catalytic Activities of Au Nanoparticles Supported on Nb_2O_5 for CO Oxidation and Furfural Oxidation, M. Lin, C. Mochizuki, T. Ishida, Y. Zhang, M. Haruta, T. Murayama, *Catal. Today* **410**, 143-149 (2023) . DOI:10.1016/j.cattod.2022.03.034
5. Selective Formation of Acetate Intermediate Prolongs Robust Ethylene Removal at 0°C for 15 Days, M. Lin, H. Wang, T. Takei, H. Miura, T. Shishido, Y. Li, J. Hu, Y. Inomata, T. Ishida, M. Haruta, G. Xiu, T. Murayama, *Nat. Commun* **14**, 2885-2892 (2023) . DOI:10.1038/s41467-023-38686-0.
6. Gold/Substituted Hydroxyapatites for Oxidative Esterification: Control of Thin Apataite Layer on Gold Based on Strong Metal-Support Interaction (SMSI) Results in High Activity, A. Taketoshi, Y. Gangarajula, R. Sodenaga, A. Nakayama, M. Okumura, N. Sakaguchi, T. Murayama, T. Shimada, S. Takagi, M. Haruta, B. Qiao, J. Wang, T. Ishida, *ACS Appl. Mater. Interrfaces* **15**, 34290-34302 (2023) . DOI:10.1021/acsami.3c05974.
7. Metal-Support Interaction in Gold Zeolitic Octahedral Metal Oxide and the Catalytic Activity for Low-Temperature Alcohol Oxidation, Y. Wang, G. Zheng, Q. Zhu, Q. Tong, B. Yu, T. Ishida, T. Murayama, Y. Li, W. Ueda, Z. Zhang, *Langmuir* **39**, 10162-10177 (2023) . DOI:10.1021/acs.langmuir.3c01095.
8. In-situ Raman Unveiled Nb-O-Bond-Dependency Selectivity for Methanol Electro-Oxidation at High Current Density, X. Wang, C. Xiao, Y. Li, T. Murayama, T. Ishida, M. Lin, G. Xiu, *Appl. Catal. A: Gen.* **664**, 119341-119350 (2023) . DOI:10.1016/j.apcata.2023.119341.
9. Au Clusters Supported on Defect-Rich Ni-Ti Oxides Derived from Ultrafine Layered Double Hydroxides (LDHs) for CO Oxidation at Ambient Temperature, A. Takahashi, A. Nakayama, T. Murayama, N. Sakaguchi, T. Shimada, S. Takagi, T. Ishida, *catalysts* **13**, 1155-1169 (2023) . DOI:10.3390/catal13081155.
10. Supported Gold Nanoparticles Prepared from NHC-Au

Complex Precursors as Reusable Heterogeneous Catalysts, Q.-A. Huang, M. Takaki, H. Murayama, A. Yoshizawa, E. Yamamoto, L. X. Dien, T. Ishida, T. Honma, N. V. Tzouras, T. Scattolin, S. P. Nolan, M. Tokunaga, *Mol. Catal.* **549**, 113460-113468 (2023) . DOI:10.1016/j.mcta.2023.113460.

11. Au/Nb_2O_5-Catalyzed *N*-Formylation of Amines Utilizing High Selectivity to Formate Intermediate in CO_2 Hydrogenation, M. Hidaka, M. Lin, H. Yamakawa, A. Nakayama, T. Murayama, T. Shimada, S. Takagi, T. Ishida, *Chem. Lett.* **52**, 874-877 (2023) . DOI:10.1246/cl.230365.
12. Low-Temperature Hydrogenation of CO_2 to Methanol in Water on ZnO-Supported CuAu Nanoalloys, J. Mosrati, T. Ishida, H. Mac, M. Al-Yusufi, T. Honma, M. Parliniska-Wojtan, Y. Kobayashi, A. Klyushin, T. Murayama, A. M. Abdel-Mageed, *Angew. Chem. Int. Ed.* **62**, e202311340-e202311350 (2023) . DOI:10.1002/anie.202311340.
13. Decoration of Gold and Platinum Nanoparticle Catalysts by 1-nm-thick Metal Oxide Overlayer and its Effect on CO Oxidation, K. Okayama, A. Nakayama, T. Murayama, N. Sakaguchi, F. Hong, B. Qiao, J. Wang, T. Shimada, S. Takagi, T. Ishida, *ACS Appl. Mater. Interfaces* **16**, 4570-4580 (2024) . DOI:10.1021/acsami.3c14935.
14. Emission Enhancement of Anthracene Derivative Caused by a Dramatic Molecular Orbital Change on the Nanosheet Surface, K. Arakawa, T. Shimada, T. Ishida, S. Takagi, W. Han, *J. Phys. Chem. C* **128**, 1995-2002 (2024) . DOI:10.1021/acs.jpcc.3c06631.
15. Structural Transformation of Azonia[5]helicene Photoproduct via Reaction Field Function of Layered Inorganic Material, K. Arakawa, T. Shimada, T. Ishida, K. Sato, S. Takagi, *Langmuir*, *in press*. DOI:10.1021/acs.langmuir.3c03589.
16. Monolayer Modification of Spherical Amorphous Silica by Clay Nanosheets, N. Nishida, K. Arakawa, T. Shimada, S. Takagi, *Langmuir*, *in press*. DOI:10.1021/acs.langmuir.3c03494.

■Invited Lectures

1. Surface-Fixation Induced Emission (S-FIE) of Organic Dyes on the Inorganic Flat Surface, S. Takagi, The 31st International Conference on Photochemistry, July, 2023, Sapporo, Japan.
2. Modification of Noble Metal Nanoparticle Surface by Thin Metal Oxide Layer Improves Catalytic Activity and Stability, T. Ishida, East China University of Science and Technology, November, 2023, Shanghai, China.
3. Modification of Gold Nanoparticle Surface by Thin Metal Oxides Aiming at Improvement of Catalytic Activity and Stability, T. Ishida, Dalian Institute of Chemical Physics, November, 2023, Dalian, China.
4. Enhanced Activity of Au Nanoparticles Covered by Hydroxyapatites, T. Ishida, International Symposium on Catalysis and Fine Chemicals (C&FC2023), December2023, Tokyo, Japan.
5. See the annual report in Japanese (1 more articles)

■Academic Meeting

＊International

1. Effect of Pt Co-Catalyst Loading Site on Photoreduction Efficiency in Titania Nanosheet, Y. Hirade, K. Fukushima, T. Shimada, S. Takagi, The 31st International Conference on Photochemistry, September, 2023, Sapporo, Japan.
2. Enhanced Fluorescence Behavior of Safranine-O by Complexing with Inorganic Clay Nanosheets, M. R. Melechalil, K. Arakawa, Y. Hirade, F. Kuttassery, T. Shimada, T. Ishida, S. Takagi, The 31st International Conference on Photochemistry, September, 2023, Sapporo, Japan.
3. Monolayer Modification of Spherical Amorphous Silica by Clay Nanosheets, N. Nishida, K. Arakawa, T. Shimada, S. Takagi, The 12th Asian Photochemistry Conference (APC) 2023, November, 2023, Melbourne, Australia.
4. Remarkable Luminescence Enhancement of Alkaloid Dyes in Aqueous Solution by Using Clay Nanosheets, H. Mori, H. Tachibana, T. Shimada, T. Ishida, S. Takagi, The 12th Asian Photochemistry Conference (APC) 2023, November, 2023, Melbourne, Australia.
5. Unique Photochemical Behavior of Dyes on The Inorganic Flat Surface, H. Mori, K. Arakawa, T. Ishida, T. Shimada, E. Hasegawa, S. Takagi, The 12th Asian Photochemistry Conference (APC) 2023, November, 2023, Melbourne, Australia.
6. Development of Supported Gold Cluster Catalysts Utilizing Layered Double Hydroxide (LDH) Nanoparticles, A. Nakayama, A. Yoshida, T. Honma, N. Sakaguchi, A. Taketoshi, T. Murayama, T. Shimada, S. Takagi, T. Ishida, EuropaCat2023, August, 2023, Prague, Czech Republic.
7. Decoration of Au/SiO_2 by Thin Metal Oxide Layer Derived from Layered Double Hydroxides (LDHs), K. Okayama, A. Nakayama, T. Murayama, N. Sakaguchi, T. Shimada, S. Takagi, T. Ishida, EuropaCat2023, August, 2023, Prague, Czech Republic.
8. Continuous transfer hydrogenolysis of THFA to 1,5-pentanediol over stable Ni-La$(OH)_3$: Towards selective synthesis of biobased a,w-diols, M. Al-Yusufi, D. Michalik, N. Steinfeldt, M. Sebek, H. Atia, R. Eckelt, C. Kubis, T. Ishida, T. Murayama, A. AbdelMageed, A. Köckritz, EuropaCat2023, August, 2023, Prague, Czech Republic.
9. Cluster-sized alloys on zeolite for robust ethylene removal at 0 °C, M. Lin, H. Wang, T. Ishida, G. Xiu, T. Murayama, EuropaCat2023, August, 2023, Prague, Czech Republic.
10. Oxidative Coupling Reaction of Dimethyl Phthalate over Supported Gold Catalysts, K. Arata, A. Nakayama, T. Murayama, T. Shimada, S. Takagi, T. Ishida, 9th Asia-Pacific Congress on Catalysis (APCAT-9), October, 2023, Hangzhou, China.
11. Catalytic Properties of Supported Gold Catalysts Utilizing Layered Double Hydroxide (LDH) Nanoparticles, A. Nakayama, A. Yoshida, T. Honma, N. Sakaguchi, T. Murayama, T. Shimada, S. Takagi, T. Ishida, 9th Asia-Pacific Congress on Catalysis (APCAT-9), October, 2023, Hangzhou, China.
12. Thin Metal Oxide Layer-Coated Au/SiO_2 Using Layered Doulble Hydroxide Nanosheets, K. Okayama, A. Nakayama, N. Sakaguchi, T. Shimada, S. Takagi, T. Ishida, 9th Asia-Pacific Congress on Catalysis (APCAT-9), October, 2023, Hangzhou, China.
13. Oxidative Homocoupling Reaction of Dimethyl Phthalate over Metal Oxide Supported Au Catalysts, K. Arata, A. Nakayama, T. Murayama, T. Shimada, S. Takagi, T. Ishida, International Symposium on Catalysis and Fine Chemicals (C&FC2023), December, 2023, Tokyo, Japan.

＊Domestic

See the annual report in Japanese (16 articles)

■Review Articles and Books

1. Supported Noble Metal Catalysts and Adsorbents with Soft Lewis Acid Functions, H. Murayama, Q-A. Huang, E. Yamamoto, M. Tokunaga, T. Ishida, M. Okumura, T. Honma, T. Fujitani, A. Isogai, *Chem. Rec.*, **23**, e202300148-e202300163(2023). (Review) DOI:10.1002/tcr.202300148.

■Awards

1. Poster Award, The 31st International Conference on Photochemistry ACS Applied Materials & Interfaces, Effect of Pt co-catalyst loading site on photoreduction efficiency in titania nanosheet
2. Excellent student presentation award, The solid and surface photochemistry conference 2023, Jiahao LU (M1), November, 2023.
3. The Best Presentation Award, Symposium on Molecular Photo-Functionalities 2023, Nanako NISHIDA (M2), December, 2023.
4. The Best Presentation Award, Symposium on Molecular Photo-Functionalities 2023, Kunpei HARAKO (M2), December, 2023.
5. The Best Presentation Award, Symposium on Molecular Photo-Functionalities 2023, Yoshinori TAHARA (M2), December, 2023.

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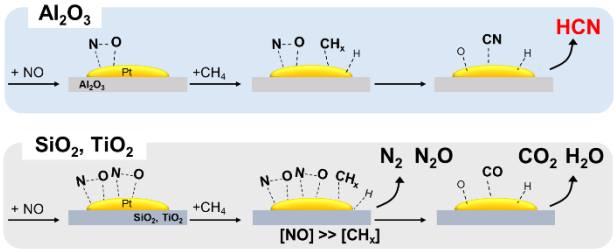
PD -1
Doctor's course -5
Master's course -8
Bachelor 4 -5

■**Outlines of the Research**

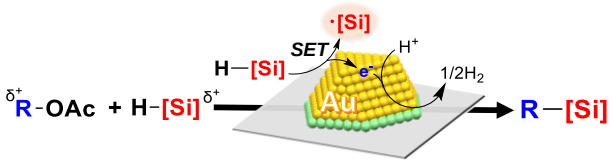
Study on the reaction of mechane and NO for the production of HCN and NH_3

Methane (CH_4) was converted to hydrogen cyanide (HCN) and ammonia (NH_3) at temperatures from 300 to 425 °C using a 5 wt% Pt/Al_2O_3 catalyst with nitric oxide (NO) as an oxidant. HCN yield of *ca.*1% was maintained even after 100 h at 400 °C. *In situ* X-ray absorption fine structure (XAFS) and Fourier-transform infrared (FTIR) spectra showed that Pt–CN species emerged, and the extent of the adsorbed species roughly correlated with the production of HCN. This study revealed that the Pt–CN species can function not only as important reaction intermediates, but also as inhibitors of the reaction. An appropriate balance of Pt–CN species and hydrogen species over the Pt surface is required to produce HCN continuously. This balance of the relative amount of adsorbed species including Pt-CN varied remarkably depending on the support.



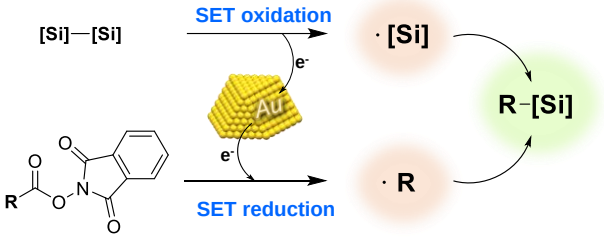
Study on the catalytic conversion of stable C–O bonds

Utilization of biomass-derived compounds attarcts much attention from the viewpoint of carbon recycling. Since biomass compounds contain many C–O bonds, the development of an efficient method for synthesizing useful compounds via direct convertion of C–O bonds. In this study, we have demonstrated that silyl cross-coupling between hydrosilanes and alkyl esters and alkyl ethers proceeded by using acidic oxide supported Au catalysts to synthesize alkylsilanes under mild conditions. This catalytic reaction enables rapid synthesis of organosilicon compounds from biomass-derived compounds and waste plastics, which will lead to the proposal of a new resource recycling system.



Study on radical nature of gold nanoparticles

Radical reactions using single-electron transfer catalysts enable organic transformations that are different from two-electron redox processes. In this study, we found that gold nanoparticles function as single-electron transfer catalysts to proceed radical coupling reactions. The corresponding alkylsilanes could be synthesized in high yield by the reaction of disilanes and redox-active esters.



■**Papers with Peer Review**

1. Acidic property and gas-phase glycerol-dehydration activity of WO_3/Al_2O_3 catalysts, Kanai, Ryuichi; Yagi, Fuyuki; Omata, Kaori; Miura, Hiroki; Shishido, Tetsuya, *Mol. Catal.*, **2023**, 113588.
2. Insights into Pt-CN Species on an Alumina-supported Platinum Catalyst as Active Intermediates or Inhibitors for Low-temperature Hydrogen Cyanide Synthesis from Methane and Nitric Oxide, Takagaki, Atsushi; Bando, Kyoko; Yamasaki, Tatsuya; Murakami, Junichi; Suganuma, Nobuya; Ghampson, Isaac Tyrone; Kodaira, Tetsuya; Ishihara, Tatsumi; Shishido, Tetsuya, *Catal. Sci. Technol.*, **2023**, *13*, 5017–5024.
3. Harnessing Supported Gold Nanoparticle as a Single-Electron Transfer Catalyst for Decarboxylative Cross-Coupling, Miura, Hiroki; Kaede, Ameyama; Shishido, Tetsuya, *Adv. Synth. Catal.*, **2023**, *365*, 62–69.
4. High-density formation of Ir/MoOx interface through hybrid clustering for chemoselective nitrostyrene hydrogenation, Hayashi, Shun; Shishido, Tetsuya, *ACS Org. Inorg. Au*, **2023**, *3*, 283–290.
5. Methane activation with nitric oxide at low temperatures on supported Pt catalysts: effects of the support, Suganuma, Nobuya; Ghampson, Isaac Tyrone; Miura, Hiroki; Murakami, Junichi; Bando, Kyoko; Kodaira, Tetsuya; Yamasaki, Tatsuya; Takagaki, Atsushi; Ishihara, Tatsumi; Shishido, Tetsuya, *Catal. Sci. Technol.*, **2023**, *13*, 3927-3939.
6. Selective formation of acetate intermediate prolongs robust ethylene removal at 0 °C for 15 days, Mingyue Lin, Haifeng Wang, TakashiTakei ,Hiroki Miura, Tetsuya

Shishido, Yuhang Li, Jinneng Hu, Yusuke Inomata, Tamao Ishida, Masatake Haruta, Guangli Xiu, Toru Murayama, *Nature Commun.*, **2023**, *14*, 2885.

7. Highly Active and Durable Rh–Mo-Based Catalyst for the NO–CO–C_3H_6–O_2 Reaction Prepared by Using Hybrid Clustering, Hayashi, Shun; Endo, Shinji; Miura, Hiroki; Shishido, Tetsuya, *ACS Materials Au*, **2023**, *3*, 456–463.
8. Deoxygenative Silylation of C(sp^3)–O Bonds with Hydrosilane by Cooperative Catalysis of Gold Nanoparticles and Solid Acids, Miura, Hiroki; Yasui, Yuki; Masaki, Yosuke; Doi, Masafumi; Shishido, Tetsuya, *ACS Catal.*, **2023**, *13*, 6787–6794.
9. Experimental Evidence for Alloying Effects in Au-Pt-catalyzed Low-temperature CH_4 Activation with NO, Ghampson, I. Tyrone; Miura, Hiroki; Murakami, Junichi; Bando, Kyoko; Kodaira, Tetsuya; Takagaki, Atsushi; Ishihara, Tatsumi; Shishido, Tetsuya, *ACS Catal.*, **2023**, *13*, 6574–6589.
10. Diverse Alkyl–Silyl Cross-Coupling via Homolysis of Unactivated C(sp^3)–O Bonds with the Cooperation of Gold and Amphoteric Oxides Miura, H.; Doi, M.; Yasui, Y.; Masaki, Y.; Nishio, H.; Shishido, T. *J. Am. Chem. Soc.* **2023**, *145*, 4613−4625
11. Inhibitory effect of trace impurities on methanol reforming by Cu/ZnO/Al_2O_3 catalyst: Steam reforming and autothermal reforming of model bio-methanol Nomoto, K.; Miura, H.; Shishido, T. *Appl. Catal. B Environ.* **2023**, *325,* 122374.
12. Low-Temperature Selective Oxidation of Methane to Methanol over a Platinum Oxide, Takagaki, A.; Tsuji, Y.; Yamasaki, T.; Kim, S.; Shishido, T.; Ishihara, T.; Yoshizawa, K. *Chem. Commun*, **2023**, *59*, 286-289.
13. Catalytic aqueous CO_2 reduction to formaldehyde at Ru surface on hydroxyl-groups-rich LDH under mild conditions, Deng, L., Wang, Z., Jiang, X., Xu, J., Zhou, Z., Li, X., You, Z., Ding, M., Shishido, T.; Liu, X.; Xu, M., *Appl. Catal. B Environ.* **2023**, *322*, 122134.

■Invited Lectures

1. Direct synthesis of lactic acid from glucose using heterogeneous catalysts
   D. Hata, K. Aihara, H. Miura, T. Shishido, The Japan Petroleum Institute 71st Annual Meeting, May 30, 2023, Tower Hall Funabori
2. Organic Synthesis on Solid Catalysts
   H. Miura, The 34th Freshman Seminar of Catalysis Society of Japan, June 3, 2023, Hongo Campus, The University of Tokyo.
3. Development of Gold and Other Element Cooperative Solid Catalysts for Highly Efficient Organic Transformations
   H. Miura, Academic Award Commemorative Lecture of Frontier Materials Research Institute July 19, 2023 at Tokyo Institute of Technology, Suzukakedai Campus
4. New Approaches of Heterogeneous Organic Synthesis by Cooperation of Different Elements
   H. Miura, 19th Workshop on Catalyst Chemistry, Shizuoka, August 3, 2023, Shizuoka City Industry-Academia Collaboration Center
5. Intermolecular Bond Formation Promoted by Cooperative Catalysis of Gold and Other Elements
   H. Miura, 132nd Annual Meeting of Catalysis Society of Japan, Hokkaido University, September 14, 2023
6. Supported Gold Nanoparticles as Single-Electron Transfer Catalysts for Cross-Coupling Reactions
   H. Miura, International Symposium on Catalysis and Fine Chemicals 2023 (C&FC2023), 5, December, 2023, Tokyo, Japan,
7. Silylation of Stable C–O bonds by Supported Gold Catalysts and the Application for Depolymerization of Polyesters
   H. Miura, Asian Polyolefin Workshop 2023 (APO2023), 13, December, 2023, Nara, Japan,
8. CO_2 Hydrogenation by Metal Phosphides Control Factors of Selectivity of CO_2 Hydrogenation
   T. Shishido, The 23rd Hokkaido Division Conference of the Japan Petroleum Institute December 21, 2023 Muroran Institute of Technology
9. Biomass Conversion Based on Dehydration Reaction by Solid Acid Catalysts
   T. Shishido , Lecture of Highly Selective Reaction Subcommittee, The Japan Association for Chemical Innovation, February 21, 2024
10. Heterogeneous Organic Synthesis Contributing to Carbon Resource Recycling
    H. Miura, 104th Annual Meeting of the Chemical Society of Japan (2024), March 21, 2024, Nihon University, Funabashi Campus.
11. Effect of Hydrogen Spillover on the Property of Solid Acids
    T. Shishido, Academic Transformation Area (B) Surface Hydrogen Engineering 6th Area Meeting, March 26-27, 2024, Shin-Yokohama International Hotel

■Academic Meeting

＊Domestic

See the annual report in Japanese (28 articles)

■Awards

1. Tokyo Institute of Technology, Institute of Innovative Research, Frontier Materials Research Institute "Development of Gold and Other Element Cooperative Solid Catalysts for Highly Efficient Organic Transformations"
   Hiroki Miura
2. Poster Award "Borylation of C(sp^3)–O Bonds of Alkyl Esters by Supported Au Catalysts"
   M. Doi, H. Miura, T. Shishido, 69th Symposium on Organometallic Chemistry
3. Poster Award "Reductive Cross-Coupling of C(sp^3)–O Electrophiles and Carbonyl Compounds by Supported Au Catalysts"
   Y. Yasui, H. Miura, T. Shishido, 69th Symposium on Organometallic Chemistry
4. Outstanding poster prize "Cooperative Catalysis between Au Nanoparticles and Metal Oxides for Rapid C–B Bond Formation"
   K. Imoto, H. Miura, A. Junkaew, M. Ehara, T. Shishido, International Symposium on Catalysis and Fine Chemicals 2023 (C&FC 2023)
5. Outstanding poster prize "Reductive Cross-Coupling of

C(sp^3)–O Electrophiles and Carbonyl Compounds by Supported Au Catalysts”
Y. Yasui, H. Miura, T. Shishido, International Symposium on Catalysis and Fine Chemicals 2023 (C&FC 2023)

6. The Japan Petroleum Institute, The Japan Petroleum Institute Award for Distinguished Papers “Particle Size Effect on Hydrogen Cyanide Synthesis with CH_4 and NO over an Alumina-supported Platinum Catalyst” Tatsuya Yamazaki, Atsushi Takagaki, Tetsuya Shishido、Kyoko, K. Bando, Tetsuya Kodaira, Jyunichi Murakami, Jun Tae Song, Eiki Niwa, Motonori Watanabe, Tatsumi Ihihara

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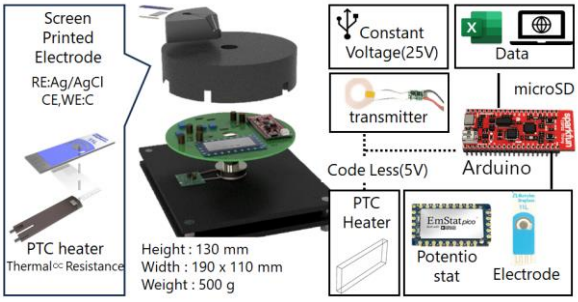
Doctor's course -3
Master's course -20
Bachelor 4 -7

■Outlines of the Research

1. Development of an Electrochemical Analysis System Using a Compact Disk-type Microfluidic Device

Hizuru NAKAJIMA, Shoji YAMAMOTO

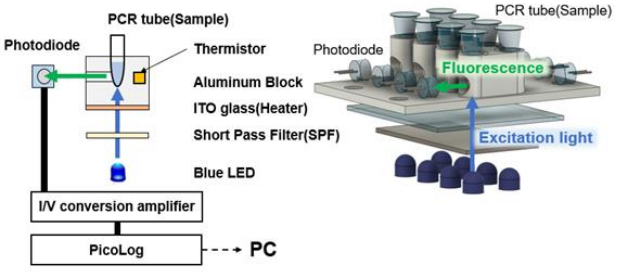
Although simultaneous measurement of multiple components and samples using microchips is highly beneficial, the need for numerous pumps and valves often results in a bulky system. To address this issue, we developed an electrochemical analysis system that utilizes a compact disc (CD)-type microchip equipped with an easily fabricated, cost-effective flow channel chip. This system uses the force generated during rotation to manipulate liquids, enabling automatic quantitative analysis of pyrophosphate ions and fully automated loop-mediated isothermal amplification (LAMP) method without relying on expensive peripherals or operational expertise. The system successfully determined positive/negative results.



2. Development of a Fluorescence Detection Genetic Testing System Based on the LAMP Method

Hizuru NAKAJIMA, Shoji YAMAMOTO

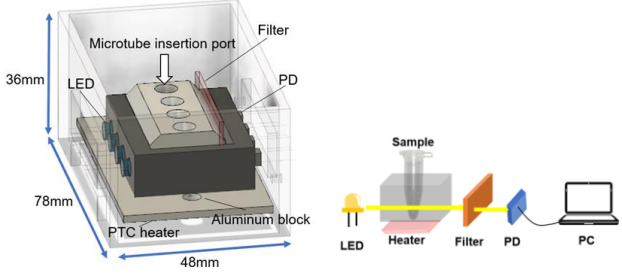
While polymerase chain reaction (PCR) methods are widely used in genetic testing, their reliance on large, expensive equipment such as thermal cyclers, electrophoresis devices, and spectrophotometers/fluorometers makes onsite testing challenging. This study introduces a novel fluorescence-based LAMP device utilizing an Indium Tin Oxide (ITO) transparent glass heater. Our device is capable of simultaneous real-time fluorescence measurement of up to eight samples. Furthermore, we demonstrated the device's ability to quantitatively analyze human genomic DNA within a concentration range of 2.11×10^2 to 2.11×10^4 ng/μL by measuring the real-time fluorescence intensity of the sample.



3. Development of an Absorbance Detection Genetic Testing System Based on the LAMP Method

Hizuru NAKAJIMA, Shoji YAMAMOTO

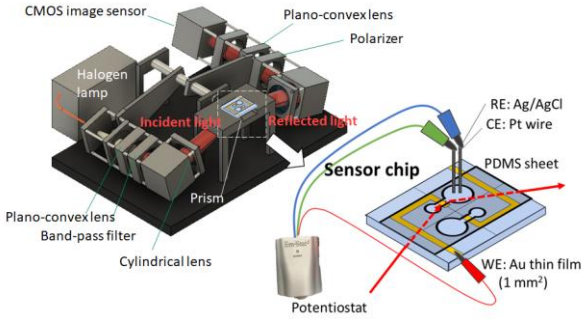
In addition to developing a genetic testing system based on fluorescence detection, we also constructed a system using absorbance detection. We successfully achieved real-time simultaneous measurement of absorbance intensity for four samples and determined positive/negative results. Furthermore, we demonstrated the capability of this system to quantitatively analyze human genomic DNA within an initial concentration range of 2.11×10^2 to 2.11×10^4 ng/μL.



4. Development of a Method for Measuring Exosomal Membrane Proteins Using SPR Sensor

Hizuru NAKAJIMA, Shoji YAMAMOTO

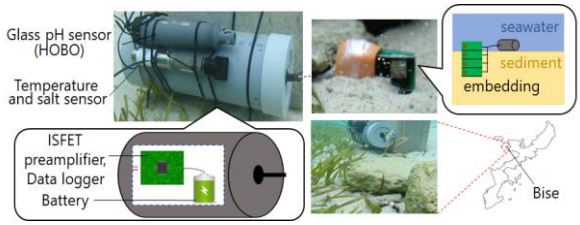
Exosomes, extracellular vesicles approximately 100 nm in diameter, contain a diverse array of proteins, making them promising tools for cancer diagnosis. In this study, we utilized a surface plasmon resonance (SPR) sensor to measure changes in the SPR signal by adding various antibodies to exosomes fused with an artificial biomembrane on the gold surface of the sensor chip. Our results successfully demonstrated real-time observation of exosome fusion to the artificial biomembrane and subsequent antibody adsorption to exosomal membrane proteins.



5. Development of a Multichannel ISFET Sensor for Measuring pH Distribution of Pore Water in Marine Sediments

Hizuru NAKAJIMA, Shoji YAMAMOTO

Recent increases in atmospheric CO_2 concentrations are accelerating ocean acidification (OA). This process impedes the formation of calcium carbonate skeletons in corals, shellfish, and other marine organisms, and may even dissolve coral reef sands, thus threatening marine life. Therefore, it is vital to measure the pH distribution in marine sediment pore water to assess the extent of OA and its impact on marine ecosystems. In this study, a multi-channel EG-ISFET sensor with a tantalum oxide ion-sensitive membrane was successfully used to observe the pH distribution and diurnal variation in marine sediments off Bise, Okinawa.



7. Measurements of VOCs at urban and suburban sites

Shungo KATO

Volatile Organic Compounds (VOCs) were observed at suburban site (Minamiosawa, Koto-ku, Kyoto). Emission sources, contribution to ozone formation of each VOC were estimated. From the comparison with NMHC analyzer, concentration of oxygenated VOC has increased in recent year.

8. Hith time resolution measurement of VOCs by SIFT-MS

Shungo KATO

Measruemnts of ambient air by SIFT-MS was conducted at urban area (Kouto-ku). From the comparison with GC-FID, the performance of SIFT-MS was examined.

9. 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.

10. Measurements of atmospheric pollutants at mountain sites

Shungo KATO

Carbon monoxide, ozone, and sulfur dioxide 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.

11. Development of volcanic gas monitoring system using small gas sensor

Shungo KATO

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

12. Hydrogen measurement in ambient air

Shungo KATO

Gas chromatography/Reduction gas detector system was constructed for low level hydrogen measurements. Atmospheric hydrogen concentration in suburban, urban, and remote sites were observed.

13. Development of microchemical pen and its applications

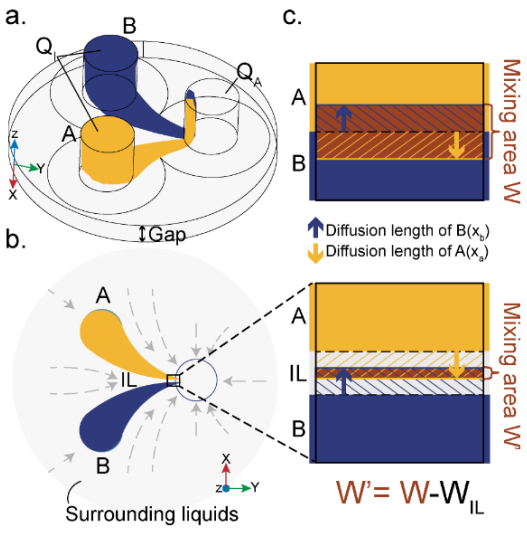
Sifeng MAO

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.

14. Insight into micro-chemical pen: microfluidic mechanism for high-resolution surface processing

Sifeng MAO

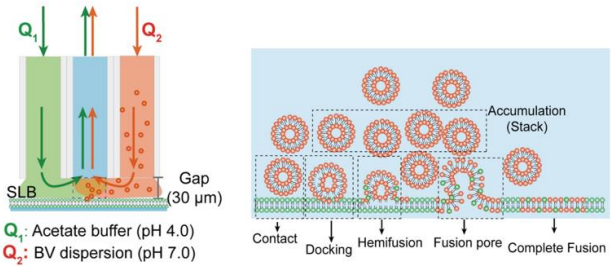
We have confirmed the existence of an intermediate layer when MCP is working, which provides MCP with extra advantages in surface processing over the conventional open-space microfluidic systems. The variation of the size of IL caused by adjusting relative parameters is further proved to be an important factor for controlling the working area.



15. Local pH control by using a laminar flow for liposome fusion control

Sifeng MAO

In this work, a laminar flow method based on a chemical pen has been proposed for local pH control. We successfully fabricated the chemical pen with two injections and one aspiration apertures, and it was demonstrated that the chemical pen can conveniently control pH condition at a defined micro-mixing region by employing different pH buffer solution as injection. Control of liposome fusion to supporting lipid bilayer was achieved.



■Papers with Peer Review

1. Hiroya Murakami, Keisuke Iida, Yuki Oda, Tomonari Umemura, Hizuru Nakajima, Yukihiro Esaka, Yoshinori Inoue, Norio Teshima
   Hydrophilic interaction chromatography-type sorbent prepared by the modification of methacrylate-base resin with polyethyleneimine for solid-phase extraction of polar compounds
   Analytical Sciences, 2023, 39_3 375-381
2. Kuizhi Qu, Kazuhiro Morioka, Konoka Nakamura, Shoji Yamamoto, Akihide Hemmi, Atsushi Shoji, Hizuru Nakajima
   Development of a C-reactive protein quantification method based on flow rate measurement of an ink solution pushed out by oxygen gas generated by catalase reaction
   Microchimica Acta, 2023, 191 24-24
3. Ryo Ishii, Sota Hirose, Shoji Yamamoto, Kazuhiro Morioka, Akihide Hemmi, Hizuru Nakajima
   Development of Portable Multi-fluorescence Detection System Using Indium Tin Oxide Heater for Loop-mediated Isothermal Amplification
   Sensors and Materials, 2024,
4. S. Itahashia, N.K. Kim, Y.P. Kim, M.J. Song, C.H. Kim, K.S. Jang, K.Y. Lee, H.J. Shin, J.Y. Ahn, J.Y. Jung, Z. Wu, J.Y. Lee, Y. Sadanaga, S. Kato, N. Tang, A. Matsuki
   Distinctive features of inorganic PM1.0 components during winter pollution events over the upwind and downwind regions in Northeast Asia
   Atmospheric Environment, 309, 119943, 2023
5. K. Shimda, Y. Geka, S. Kato, C. K. Chan, Y. P. Kim, C.-F. Ou-Yang, N.-H. Lin, S. Hatakeyama
   Possibility of condensation of nitric acid for cloud condensation nucleus in the summer at Mt. Fuji
   Atmospheric pollution Research, 15, 101940, 2024
6. Jianmin Yang, Yuxiang He, Zhendong Li, Xudong Yang, Yueming Gao, Mingmao Chen, Yunquan Zheng, Sifeng Mao, Xianai Shi
   Intelligent wound dressing for simultaneous in situ detection and elimination of pathogenic bacteria
   Acta Biomaterialia, 174, 177-190, 2024.
7. Anchen Fu, Sifeng Mao, Nahoko Kasai, Haiyan Zhu, Hulie Zeng
   Dynamic tissue model in vitro and its application for assessment of microplastics-induced toxicity to air-blood barrier (ABB)
   Biosensors and Bioelectronics, 246, 115858, 2024.
8. Sifeng Mao
   Recent advances in nanowire sensor assembly using laminar flow in open space
   TrAC Trends in Analytical Chemistry, 159, 116918, 2023.

■Invited Lectures

■Academic Meeting

＊International

1. Shungo Kato
   Long-term measurements of trace gases at the summit of Mt. Fuji during summer
   ACID RAIN 2020， 2023/4/19 Toki Messe・Niigata Convention Center, S3A-3
2. Kazuhiro Morioka, Toshimasa Miyawaki, Kenta Suzuki, Nori Fujita, Shoji Yamamoto, Hizuru Nakajima, Akihide Hemmi, Hajime Kayanne
   Microfluidic-Based ISFET Sensor Using Carbon Fiber Tape for Monitoring of Seawater pH
   PITTCON2024, 2024/2/26 San Diego Convention Center USA, PS-E266
3. Sota Hirose, Ryo Ishii, Shoji Yamamoto, Kazuhiro Morioka, Akihide Hemmi, Hizuru Nakajima
   Development of a portable genetic testing device based on fluorescence detection using the LAMP method
   PITTCON2024, 2024/2/27 San Diego Convention Center USA, PS-I111
4. Sifeng Mao
   Microchemical Pen: Microfluidic approach for single cell analysis
   Beijing Conference and Exhibition on Instrumental Analysis 2023, 2023/9/8 , Beijing, China
5. Sifeng Mao
   Real-time electrochemical detection of lactate response from single cell
   Advances in Pharmaceutical Analysis 2023/11/10-12, Beijing, China

＊Domestic

See the annual report in Japanese (24 articles)

■Books

■Awards

See the annual report in Japanese (1 articles)

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Master's course -4
Bachelor 4 -1

■Outlines of the Research

1. Research on Homogeneous Charge Compression Ignition Combustion.
Internal combustion engines have advantages over polymer electrolyte fuel cells in terms of power output and durability. This study analyzed homogeneous charge compression ignition combustion, which is expected to be a new combustion method for increasing the efficiency of internal combustion engines, using elementary reaction numerical simulations. Auto-ignition control by fuel reforming using engine exhaust heat is also studied.

2. Research on closed-cycle hydrogen engine
The Argon circulation closed-cycle hydrogen engine is expected to have high theoretical thermal efficiency due to the high specific heat ratio of the working fluid. In this study, the feasibility of a closed-cycle hydrogen engine with argon circulation using homogeneous charge compression ignition, which has not been reported in the past, is analyzed using elementary reaction numerical simulations.

3. Performance improvement in polymer electrolyte fuel cell.
Polymer electrolyte fuel cells have an advantage over internal combustion engines in terms of theoretical efficiency but a disadvantage in terms of power output. This research is to improve the power output of PEFCs, mainly by improving the reactant supply channel to reduce diffusion polarization. An electrochemical hydrogen compression system using the same cell is also studied.

4. Performance improvement in direct methanol fuel cell.
Direct methanol fuel cells have the advantage of high fuel energy density, but they are inferior to polymer electrolyte fuel cells in terms of power output. This research investigates the effect of porous metal flow field for enhancing the reactant supply and product removal at the electrodes.

■Papers with Peer Review

See the annual report in Japanese

■Academic Meeting

＊Domestic

See the annual report in Japanese

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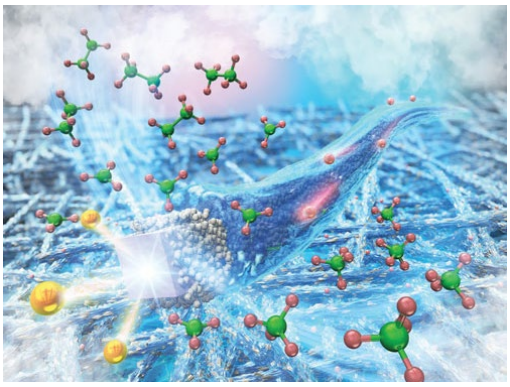
Specially Appointed Associate Professor - 1
Postdoctoral Researcher - 1
Doctor's course - 2
Master's course - 4
Bachelor (4th year) - 3
Research student - 1

■**Outlines of the Research**

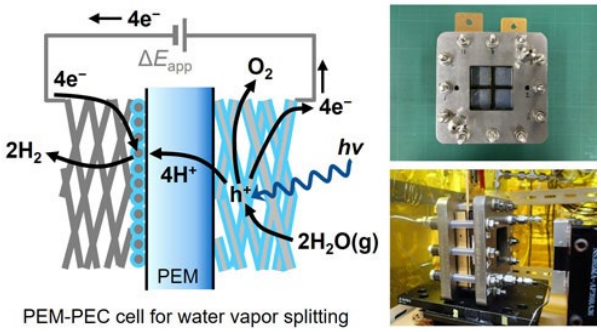
1. Photoelectrochemical methane conversion

We developed a continuous gas-fed photoelectrochemical (PEC) system with a proton exchange membrane for CH_4 activation at ambient temperature and pressure. We found that both water splitting and steam reforming of CH_4 were induced over oxide photoanodes. When the CH_4 concentration was low, O_2 and CO_2 were formed on titanium oxide (TiO_2) and tungsten trioxide (WO_3) photoanodes under ultraviolet light irradiation. We also found that visible light enhanced CH_4 activation and ethane (C_2H_6) formation over the WO_3 photoanode. When the CH_4 concentration increased, O_2 formation was suppressed, with increasing production rates of CO_2, C_2H_6, and CO. Under optimized conditions, the selectivity of C_2H_6 reached 57% on a carbon basis over the WO_3 photoanode under visible-light irradiation. The production of C_2H_6 implies the formation of methyl radicals during the CH_4 gas-fed PEC process. We also demonstrated the PEC coupling of ethane to *n*-butane and the visible-light-induced oxidation of CH_4 without external bias.



2. Proton exchange membrane PEC water splitting

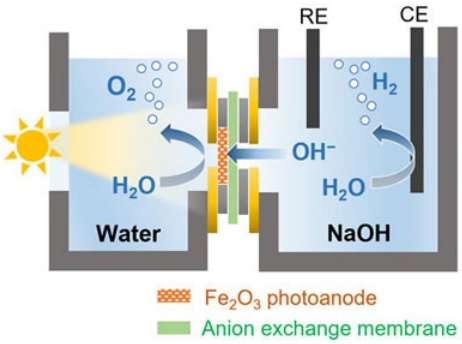
We developed vapor-fed PEC systems specifically designed for utilizing water vapor as a hydrogen resource. The PEC system under water vapor feeding utilizes a proton exchange membrane as a solid polymer electrolyte. Additionally, it utilizes gas-diffusion photoelectrodes composed of a fibrous conductive substrate with macroporous structures. Herein, the porous photoelectrodes are composed of n-type oxides for oxygen evolution reactions and used with a Pt electrocatalyst cathode for hydrogen evolution reactions. Based on the conceptual framework of vapor-fed PEC hydrogen production and strategic design of gas-phase PEC reaction interfaces, we developed porous photoanodes such as TiO_2, WO_3, strontium titanate ($SrTiO_3$), and bismuth vanadate ($BiVO_4$). A significant enhancement in the PEC efficiency was achieved through the application of a thin proton-conducting ionomer film on these porous photoelectrodes for surface functionalization. The rational design of proton exchange membrane-based PEC cells will play a pivotal role in realizing renewable-energy-driven hydrogen production from atmospheric humidity in the air.



PEM-PEC cell for water vapor splitting

3. Anion exchange membrane PEC water splitting

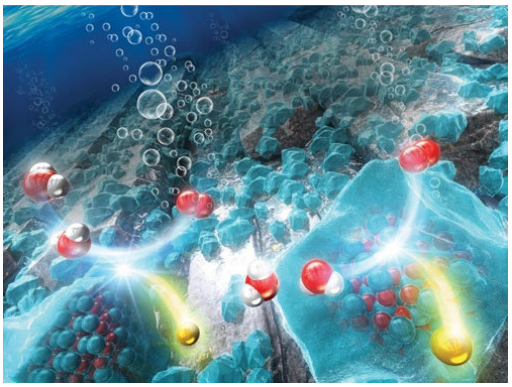
The requirement for liquid electrolytes to maintain their ionic conductivity hinders the practical implementation of PEC systems. We fabricated membrane electrode assembly by incorporating porous α-Fe_2O_3 (hematite)-based photoanodes with an anion-exchange membrane (AEM). We demonstrated AEM–PEC water splitting in pure water without supporting electrolytes over porous hematite photoanodes under visible-light irradiation. This PEC system was operational even under low conductivity and near-neutral conditions (~1 mS/m and pH ~9). Action spectral analysis confirmed a visible-light response extending up to 600 nm, surpassing that of previously reported photoelectrodes with solid-electrolyte membranes.



4. Electrocatalysts for water electrolysis

Ruthenium oxide (RuO_2) electrocatalysts possessing high activity and stability are needed to sustain the oxygen evolution reaction (OER) under harsh anodic conditions in acidic water electrolysis systems. We explored the activity and stability of RuO_2 particles coated on a Ti-fiber felt substrate. Amorphous RuO_2 particles of low crystallinity exhibited large electrochemically active surface areas (ECSAs) and high OER activity but were unstable during the OER in 0.1 M H_2SO_4. However, the complete thermal decomposition of a $RuCl_3$ precursor solution at temperatures above 250 °C yielded RuO_2 particles with enhanced crystallinity and greater resistance to dissolution under anodic conditions in H_2SO_4. An optimum calcination temperature of 350 °C produced RuO_2 nanoparticles on a Ti-felt with balanced ECSAs and high crystallinity, while simultaneously achieving high OER activity and enhanced

stability. The optimized nanocrystalline RuO_2/Ti-felt(350) electrocatalyst was stable throughout 48 h of operation at 50 mA cm^{-2} at pH 1.0 and delivered a stability number greater than 1×10^5, which is comparable to the value provided by more costly IrO_2 electrocatalysts.



■Papers with Peer Review

1. F. Amano*, S. Nomura, C. Tateishi, S. Nakayama, Clarification of Photoelectrochemical Oxygen Evolution Sites in TiO_2 Nanotube Array Electrodes by PbO_2 Deposition Method, *Journal of The Electrochemical Society*, 170, Article 026501, 2023
2. D.O.B. Apriandanu, S. Nakayama, K. Shibata, F. Amano*, "Ti-doped Fe_2O_3 Photoanodes on Three-Dimensional Titanium Microfiber Felt Substrate for Photoelectrochemical Oxygen Evolution Reaction", *Electrochimica Acta*, 456, Article 142434, 2023
3. J.J.M. Vequizo, K. Kato, F. Amano, and A. Yamakata*, "Unfolding the Impact of H_2-Reduction Treatment in Enhancing the Photocatalytic Activity of Rutile TiO_2 Based on Photocarriers Dynamics", *The Journal of Physical Chemistry C*, 127(22), pp 10411–10418, 2023
4. F. Amano*, A. Shintani, T. Sakakura, Y. Takatsuji, T. Haruyama, "Photoelectrochemical C–H Activation of Methane to Methyl Radical at Room Temperature", *Catalysis Science & Technology*, 13(16), pp 4640–4645, 2023
5. D.O.B. Apriandanu, R.M. Surya, K. Beppu, F. Amano*, "Anion Exchange Membrane Photoelectrochemical Water Splitting Using Porous Hematite Photoanodes", *ACS Applied Energy Materials*, 6(21), pp 10736–10741, 2023
6. K. Beppu, K. Obigane, F. Amano*, "Amorphous versus Nanocrystalline RuO_2 Electrocatalysts: Activity and Stability for Oxygen Evolution Reaction in Sulfuric Acid", *Catalysis Science & Technology*, 13, pp 6653–6661, 2023
7. F. Amano*, A. Ishikawa, H. Sato, C. Akamoto, S.P. Singh, S. Yamazoe, T. Sugimoto, "Facilitating Methane Conversion and Hydrogen Evolution on Platinized Gallium Oxide Photocatalyst through Liquid-like Water Nanofilm Formation", *Catalysis Today*, 426(15), Article 114375, 2024
8. F. Amano*, K. Tsushiro, "Proton Exchange Membrane Photoelectrochemical Cell for Water Splitting under Vapor Feeding", *Energy Materials*, 4, Article 400006, 2024, Mini Review, *Special Issue in Interface Engineering in (Photo)electrochemical Systems*
9. T. Yamamoto*, S. Kawaguchi, T. Kosuge, A. Sugai, N. Tsunoda, Y. Kumagai, K. Beppu, T. Ohmi, T. Nagase, K. Higashi, K. Kato, K. Nitta, T. Uruga, S. Yamazoe, F. Oba, T. Tanaka, M. Azuma, S. Hosokawa*, "Emergence of Dynamically-Disordered Phases During Fast Oxygen Deintercalation Reaction of Layered Perovskite", *Advanced Science*, 10(19), Article 2301876, 2023

■Reviews

＊Domestic

See the annual report in Japanese (1 article)

■Invited Lectures

＊International

1. F. Amano, Proton exchange membrane photoelectrochemical cell and gas-diffusion photoanodes for vapor-fed water splitting, *The Annual Nanotechnology Conference 2023*, August 27–30, 2023, Warsaw, Poland, Invited Talks

＊Domestic

See the annual report in Japanese (2 lectures)

■Academic Meeting

＊International

1. F. Amano, S. Nakayama, and K. Beppu, Activation of Methane Mediated by Water Molecules on the Surface of Semiconductor Photocatalysts, *The 19th Korea-Japan Symposium on Catalysis*, May 15–17, 2023, Seoul, Korea, Oral presentation
2. D.O.B. Apriandanu, R.M. Surya, and F. Amano, Anion Exchange Membrane Photoelectrochemical Water Splitting Using Porous Hematite Photoanodes, *The 19th Korea-Japan Symposium on Catalysis*, May 15–17, 2023, Seoul, Korea, Oral presentation (Oral Presentation Award)
3. R.M. Surya, D.O.B. Apriandanu, K. Beppu, and Fumiaki Amano, Surface Modification of Macroporous Cu_2O Photocathode for Hydrogen Evolution Reaction, *The 19th Korea-Japan Symposium on Catalysis*, May 15–17, 2023, Seoul, Korea, Poster presentation
4. F. Amano, S. Nakayama, and K. Beppu, Photocatalytic Dehydrogenative Coupling of Methane Mediated by Water Molecules on Semiconductor Photocatalysts, *The Annual Nanotechnology Conference 2023*, August 27–30, 2023, Warsaw, Poland, Poster presentation

＊Domestic

See the annual report in Japanese (22 presentations)

Applied Chemistry Colloquium

400th 2023/09/08

Akihiko Kikuchi (Tokyo University of Science)

" Thermo-Responsive Polymers for Biomaterials "

401st 2023/09/22

Makoto Tokunaga (Department of Chemistry, Graduate School of Science, Kyushu University)

" Novel Topics in Sulfur Chemistry — Adsorption and Decomposition Desulfurization, Synthesis of sulfanes using hydrogen instead of hydrogen sulfide "

402nd 2024/01/23

Shigehiro Yamaguchi (Nagoya University)

" Main-Group-Rich π-Electron Materials: Design and Application "

403rd 2023/11/10

Hiroshi Yanagi (Graduate Faculty of Interdisciplinary Research, Faculty of Engineering, Materials Science, University of Yamanashi)

" Material design guidelines and practices for oxide-based semiconductor materials "

404th 2023/12/21

Ikuhiko NAKASE (Department of Biological Chemistry, Graduate School of Science, Osaka Metropolitan University)

" Development of drug delivery systems using extracellular vesicles and effective use of functional peptides "

405th 2024/01/22

Ali M. Abdel-Mageed (Surface Chemistry in Applied Catalysis, Leibniz Institute for Catalysis, Germany)

" Catalysis on Heterogeneous Single-Atom Catalysts Supported by Metal-Organic Frameworks-Opportunities and Challenges "

Annual Report 2023

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