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 2022

Department of Applied Chemistry for Environment

Index

Reports from Research Groups

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■**Outlines of the Research**

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

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

This year, we developed new surface-modified silica nanoparticles and evaluated composite membranes containing these particles. The composite membranes containing 50wt% particles showed excellent toughness. In addition, the gas permeability of the composite membrane was 5 to 10 times higher than that of the matrix polymer, indicating that the composite membrane has better gas permeability than previous composite membranes.

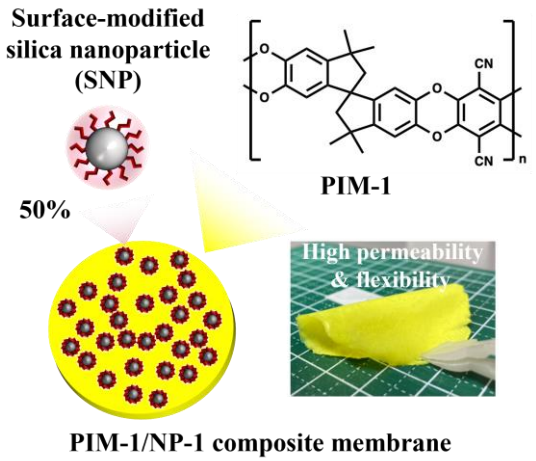

Figure 1. Schematic drawing of nanoparticle/PIM-1 composite membrane.

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

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

In this year, we studied the stability of polymer electro membranes for long-term durability of polymer electrolyte fuel cells. Most polymer electrolytes, including Nafion®, are known to be degraded by reactive radicals generated by gas crossover through the membranes (Fig.2). The Fenton tests were attempted to analyze chemical degradation of the polymer electrolyte membranes. As a result, the nanofiber composite membranes, especially composite membranes based on blend nanofibers consisted of sulfonated polymers and basic polymers, showed higher chemical stabilities than the membrane without nanofibers. In addition, the membrane fabrication processes were also investigated for practical realization of fuel cells using the nanofiber composite membranes.

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

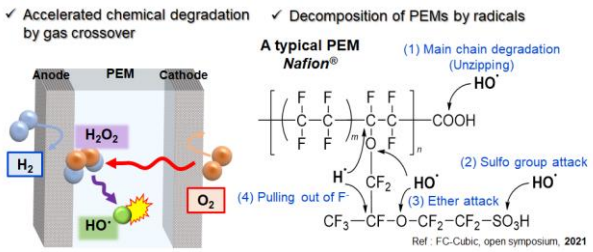

Figure 2. Chemical degradation mechanism of polymer electrolyte membranes.

3. Study of Electrospun Nanofibers

Hiroyoshi KAWAKAMI, Manabu TANAKA

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

In this year, we developed polymer nanofiber composite membranes for all solid state secondary batteries. The novel polymer composite membranes consisted of poly(vinyl ethylene carbonate) (PVEC)-based matrix polymer electrolytes, instead of conventional poly(ethylene oxide) (POE)-based one, were fabricated by combining the electrospun polymer nanofibers. The novel nanofiber composite membranes showed significantly high ion conductivity above 10^{-3} S/cm at room temperature, indicating the high potential of the nanofiber composite membranes for high-performance secondary batteries.

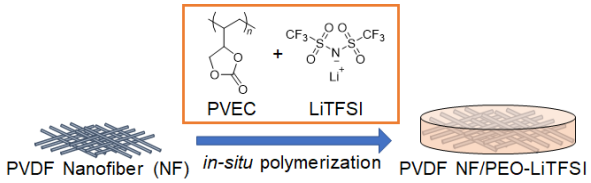

Figure 3. Schematic illustration of lithium ion conductive polymer nanofiber composite membrane for all solid state lithium ion batteries.

4. Catalysts for Electrochemical CO_2 Reduction

Hiroyoshi KAWAKAMI, Kiyoshi SATO, Toyotaka NAKAE

Electrochemical CO_2 reduction is one of the promising methods for CO_2 conversion into fuels or valuable raw materials for chemical products form recovered CO_2 emitted by factories, offices, commercial facilities, and households or exist in the atmosphere. However, an effective catalyst with both product selectivity and ability to suppress O_2 reduction and H_2 generation has yet to be found.

In this year, we have prepared catalyst-modified electrodes fabricated by drop-cast deposition of metal oxide nanoparticle onto copper nanocrystals. The catalyst-modified electrodes suppress the competitive reactions, i.e. O_2 reduction and H_2 evolution, and improve the C2/C1 product selectivity provably due to maintain the oxidative state of Cu surface. Further improvement of the catalytic activity and the product selectivity is under investigation.

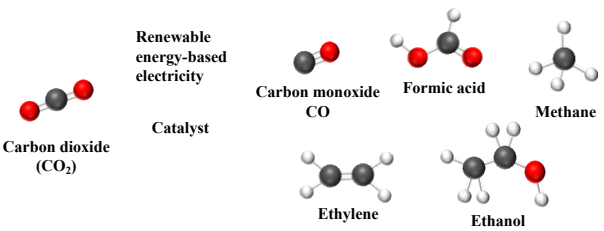

Figure 4. CO_2 conversion by electrochemical CO_2 reduction catalyst.

5. 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.

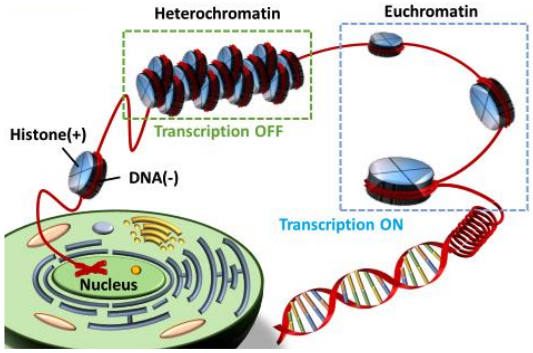

Figure 5. Gene expression control through chromatin modifications.

6. Suppression of Cellular Senescence

Hiroyoshi KAWAKAMI, Kiyoshi SATO, Masahiro YOSHIOKA

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.

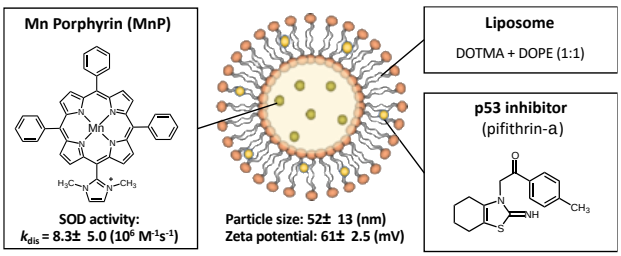

Figure 6. Structure of mitophagy-induced liposomal nanocarrier.

7. Processing of feeble magnetic materials under a magnetic field

Masafumi YAMATO

Controls of higher-order structure of feeble magnetic materials by using a magnetic field have been studied in order to

improve some properties and to reveal new functions of the materials.

This year, we investigated the magnetic orientation of hydrotalcite, which is one of the layered double hydroxides. It was found that the c-axis of hydrotalcite is oriented perpendicular to the magnetic field. This result indicates that the anisotropy of hydrotalcite composite films can be controlled by using a magnetic field.

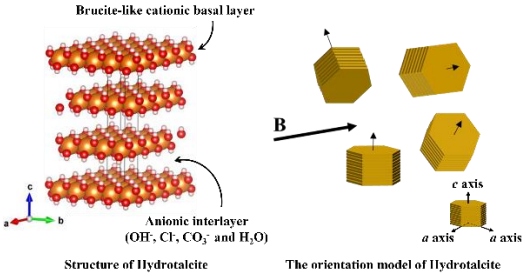

Figure 7. Crystal structure of hydrotalcite (left) and schematic drawing of magnetic orientation (right).

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. Masafumi Yamato, Ayano Imai, Hiroyoshi Kawakami, "Thermal properties of polymer with intrinsic microporosity membranes", *Polymer*, **259**, 125339 (2022). DOI: 10.1016/j.polymer.2022.125339
2. Yuta Yoshimoto, Yuiko Tomita, Kohei Sato, Shiori, Higashi, Masafumi Yamato, Shu Takagi, Hiroyoshi Kawakami, Ikuya Kinefuchi, "Gas Adsorption and Diffusion Behaviors in Interfacial Systems Composed of a Polymer of Intrinsic Microporosity and Amorphous Silica: A Molecular Simulation Study", Langmuir, 38, 7567-7570 (2022)
3. Yuri Nara, Manabu Tanaka, Kensaku Nagasawa, Yoshiyuki Kuroda, Shigenori Mitsushima, Hiroyoshi Kawakami, "Development of highly alkaline stable anion conductive polymers with fluorene backbone for water electrolysis", *Polymers for Advanced Technology*, **33**, 2863-2871 (2022) DOI: doi/full/10.1002/pat.5752
4. Manjit Singh Grewal, Manabu Tanaka, Hiroyoshi Kawakami, Solvated Ionic-Liquid Incorporated Soft Flexible Cross-Linked Network Polymer Electrolytes for Safer Lithium Ion Secondary Batteries, *Macromolecular Chemistry and Physics*, **223**, 2100317 (2022). DOI: 10.1002/macp.202100317
5. Kazushi Enomoto, Kotaro Takeda, Naoto Iwata, Kiyohiro Adachi, Tomoka Kikitsu, Yasuhiro Ishida, Daisuke Hashizume, Manabu Tanaka, Hiroyoshi Kawakami, and Yong-Jin Pu, "Colloidal CdS Quantum Dot Fibers Prepared by Electrospinning of Their Wet Gel for Quantum Nanowires", *ACS Applied Nano Materials*, **5**, 3756-3762 (2022) DOI: 10.1021/acsanm.1c04403
6. 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*, Advance online publication (2022). DOI: 10.1007/s10047-022-01356-x
7. Kazuma Komine, Takashi Nakaoji, Masafumi Yamato, Magnetic Orientation of Liquid Crystalline Montmorillonite in Ionic Liquids, *Chemistry Letters*, **51**, 1008 (2022). DOI:
8. 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 (2022)
9. Yasuko Noritomi, Takashi Kuboki, Hidetaka Noritomi, "Promotion of the Redox Reaction at Horseradish Peroxidase Modified Electrode Combined with Ionic Liquids under Irreversible Electrochemical Conditions", Results in Chemistry,4, 100666 (2022)
10. Hiroto Miyabe, Mizuha Ujita, Masaki Nishio, Toyotaka Nakae, Tsukasa Usuki, Minako Ikeya, Chika Nishimoto, Suguru Ito, Mineyuki Hattori, Satoshi Takeya, Shigenobu Hayashi, Daisuke Saito, Masako Kato, Hiroshi Nishihara, Teppei Yamada, Yoshinori Yamanoi "A series of D–A–D structured disilane-bridged triads: structure and stimuli-responsive luminescence studies" The Journal of Organic Chemistry, 87, 8928–8938 (2022). DOI: 10.1021/acs.joc.2c00641
11. Masahiro Yoshioka, Rio Matama, Mayu Miyoshi, Momoka Chatani, Akiko Takenouchi, Yuichi Kinoshita, Yoshiharu Okamoto, Katsuhiko Yoshizawa, "Evaluation of Chitosan Oligosaccharide Supplementation in Breast Cancer using In Vitro and In Vivo model.", Basic Investigation of Breast Carcinoma, 29, 39-45 (2022) (in Japanese)
12. Akiko Takenouchi, Risa Enomoto, Yuka Horikawa, Chihiro Koyama, Masahiro Yoshioka, Takafumi Iguchi, Kazuhiko Yamashita, Yoshiharu Okamoto, Katsuhiko Yoshizawa, "Effects of Sake-Lees-Derived Profine® Supplementation In Rat Models of Acute Hepatic Injury", Functional Food Research, 17, 166-176 (2022) (in Japanese)
13. Momoka Chatani, Naomi Saito, Masahiro Yoshioka, Yuichi Kinoshita, Hanae Nakamura, Yuki Hashimoto, Akiko Takenouchi, Katsuhiko Yoshizawa, "Pathophysiological Inhibitory Effect of Acerola in N-Methyl-N-Nitrosourea-Induced Cataract Rat Model", New Food Industry, 65, 3, 143-151 (2023) (in Japanese)

■Books

1. Kiyoshi Sato, Hiroyoshi Kawakami, "Treatment of Cellular Senescence with Functional Nanoparticles Restoring Mitochondrial Quality Control System ― Rejuvenation of Senescent Cells by Reactivation of Mitophagy―", The CELL, 55 (2), 111-114 (2023) (in Japanese)
2. Kiyoshi Sato, Hiroyoshi Kawakami, "Engineering Exosomes – A New Platform in Therapeutics", Chemistry, 78 (3), 66-67 (2023) (in Japanese)
3. Masafumi Yamato, Kazuma Komine, Kohki Takahashi,

Development of anisotropic gel with nano-expander structure, 2022 Annual report of high field laboratory for superconducting materials in institute for materials research at Tohoku university, p.p. 152-153 (2022) (in Japanese)

4. Hidetaka Noritomi, Biochar: Characterization and Applications in Enzyme Technology, Durham, United States, Generis Publishing (2022)

■Invited Lectures

1. Hiroyoshi Kawakami, Development of ultra-high CO_2 permeable separation membranes for CCS- and DAC-oriented strategies, SPSJ, June 2022, Online (in Japanese).
2. Hiroyoshi Ionic conductive polymer nanofibers that improve battery performance, SPSJ Webiner, July 20212, Online (in Japanese).
3. Hiroyoshi Kawakami, Development of polymer materials realizes "decarbonization", 71th Polymer Symposium in Japan, September 2022 (Hokkaido Univ.), September 2022, (in Japanease).
4. Hiroyoshi Kawakami, Cell rejuvenation by nanocarrier, Cosme Tech 2022 Tokyo (Tokyo), January 2022 (in Japanese).
5. Hiroyoshi Kawakami, Development of electrolyte membranes for fuel cells required after 2030s and 2040s, Special lecture at Iwate University (Morioka), January 2023, (in Japanese).
6. Hiroyoshi Kawakami, Functional membranes that control H2 and CO2 - H2O2 control leads to next-generation infectious disease treatment -, Kobe University, Membrane Technology (Hobe), March 2023 (in Japanese).
7. Kiyoshi Sato, “Potential of metalloporphyrin and copper catalysts for electrochemical CO2 reduction", Technical Information Institute seminar "CO2 catalysts", May 2022 (Online) (in Japanease)
8. Manabu Tanaka, Hiroyoshi Kawakami, Electrolyte Membrane Applications of Electrospun Polymer Nanofibers to Improve Fuel Cell and Battery Performances, The Annual Meeting of the Society of Fiber Science and Technology (Tokyo), June 2022 (in Japanese)
9. Manabu Tanaka, Development of Battery Materials Based on Organic Nanoionics, Summer Seminar for Young Researchers, Society of Polymer Science Japan, Tohoku Division (Online), July 2022 (in Japanese).
10. Masafumi Yamato, Thermal and magnetic properties of polymer, 2022 Basic seminar of polymer science for young engineers, Dec. 2022, Tokyo, Japan (in Japanese).
11. Masafumi Yamato, Higher-order structure analysis of macromolecules, Characterization seminar for macromolecules 2022, Mar. 2023, Online (in Japanese)
12. Masafumi Yamato, Tokyo Metropolitan University x Kansai University "~Considering the Future Global Environment~" Online Environmental Symposium, Mar. 2023, Online (in Japanese)

■Academic Meeting

1. Yasutaka Kuwahara, Kazuma Komine, Toyotaka Nakae, Hiroyoshi Kawakami, Fabrication and properties of crosslinked-PVA nanofiber-framework composite membrane for fuel cell, The 71th SPSJ Annual Meeting, (Online), 2P1C012, May 2022 (in Japanese)
2. Mizuki Akatsuka, Masafumi Yamato, Hiroyoshi Kawakami, Gas permeation property of PIM-1 membrane at high temperature, 71th SPSI Annual Meeting (Online Virtual Meeting), 2P3D017, May 2022 (in Japanese).
3. Kaito Udo, Masafumi Yamato, Hiroyoshi Kawakami, Fabrication and gas permeation properties of gas separation membranes based on nanofiber framework, 71th SPSI Annual Meeting (Online Virtual Meeting), 2P1E013, May 2022 (in Japanese).
4. Kenta Sando, Nohara Yokota, Manabu Tanaka, Hiroyoshi Kawakami, Fabrication and evaluation of polymer nanofiber composite electrolyte membranes with various lithium salt concentrations, The 71st SPSJ Annual Meeting (Online), 2PA018, May 2022 (in Japanese)
5. Kohei Shibusawa, Koki Mino, Keisuke Ashiba, Kiyoshi Sato and Hiroyoshi Kawakami, Restoration of mitochondrial quality control mechanism in senescent stem cells by mitophagy-inducing nanocarriers., The 71th SPSJ Annual Meeting (Online), 3P4B046 May 2022 (in Japanese)
6. Ryota Inahara, Kazuto Suzuki, Manabu Tanaka, Hiroyoshi Kawakami, Fabrication and fuel cell evaluation of composite electrolyte membranes composed of acid/basic blend nanofibers for higher proton conductivity at high temperature and under low humidity, The 29th Fuel Cell Symposium (Tower Hall Funabori), No.11 May 2022 (in Japanese)
7. Mizuki Akatsuka, Masafumi Yamato, Hiroyoshi Kawakami, Temperature dependence of gas permeability of PIM-1 composite membrane with surface-modified silica nanoparticles., 44th annual meeting of membrane science of Japan, June 2021, P-118S, (Online) (in Japanease).
8. Kaito Udo, Masafumi Yamato, Hiroyoshi Kawakami, Gas permeation properties of composite membranes consisted of PIM-1 and nanofiber framework, 44th annual meeting of membrane science of Japan, June 2021, P-125, (Online) (in Japanease).
9. Ryota Inahara, Kazuto Suzuki, Manabu Tanaka, Hiroyoshi Kawakami, Fabrication and evaluation of composite electrolyte membranes composed of acid/basic blend polymer nanofibers for fuel cell operation over wide temperature range, The Annual Meeting of the Society of Fiber Science and Technology (Hybrid), IC07 June 2022 (in Japanese)
10. Kenta Sando, Nohara Yokota, Manabu Tanaka, Hiroyoshi Kawakami, The effects of lithium salt concentration on secondary battery properties of polymer nanofiber composite electrolyte membranes, The Annual Meeting of the society of fiber science and technology Japan (Tower Hall Funabori, On-site & Online), 1C09, June 2022 (in Japanese)
11. Kota Iwasaki, Manabu Tanaka, Hiroyoshi Kawakami, Fabrication and evaluation of acid-functionalized and polydopamine-modified nanofibers for fuel cell application, The Annual Meeting of the society of fiber science and technology Japan, 1PA207, June 2022 (in Japanese)
12. Kota Iwasaki, Manabu Tanaka, Hiroyoshi Kawakami, Introduction of acid functional groups to nanofiber surface by in-situ polymerization and fabrication of nanofiber

composite electrolyte membranes, The Annual Meeting of the society of fiber science and technology Japan, 1C08, June 2022 (in Japanese)

13. Shuntarou Kimura, Hiroyoshi Kawakami, Induction of cellular senescence in cancer cells using epigenetics control carriers, The 26th Annual Meeting of the Japanese Association for Molecular Target Therapy of Cancer（ISHIKAWA ONGAKUDO）, P3-5（June 2022）
14. Mizuki Akatsuka, Masafumi Yamato, Hiroyoshi Kawakami, Temperature dependence of gas permeability for mixed matrix membranes composed of PIM-1 and surface-modified silica nanoparticles, The 13th conference of the Aseanian Membrane Society, (Online), P01, July 2022.
15. Kazuma Komine, Takashi Nakaoji, Masafumi Yamato, and Kawakami Hiroyoshi, Anisotropic properties of Liquid Crystal comprising Clay and Ionic Liquid., IUMRS-ICYRAM2022, (Online), A-O3-013, August 2022.
16. Yuri Nara, Manabu Tanaka, Hiroyoshi Kawakami, Synthesis and Water Electrolysis Evaluation of Anion Conductive Polymers Bearing no heteroatoms in the polymer main chains, 2022 ReHES Workshop(after the lecture meeting by Prof. Dario R. Dekel), (Tokyo Metropolitan University), A20, September 2022.
17. Kiyoshi Sato, Koki Mino, Ayaka Mori, Keisuke Ashiba, Masahiro Yoshioka, Hiroyoshi Kawakami, "Liposomal nanoparticles for maintaining cell quality", 71st Polymer Symposium in Japan, September 2022 (Sapporo) (in Japanease).
18. Manabu Tanaka, Nohara Yokota, Kenta Sando, Ryodai Fujihashi, Hiroyoshi Kawakami, Development of polymer nanofiber-based composite electrolyte membranes and evaluation of the lithium ion conduction mechanism in the composite membranes, 71th Polymer Symposium in Japan, September 2022 (Hokkaido Univ.) (in Japanease)
19. Masafumi Yamato, Shiori Higashi, Hiroyoshi Kawakami, Structure and Gas Permeation Properties of Highly Concentrated Silica Composite Membrane, 71st Polymer Symposium in Japan, September 2022 (Sapporo) (in Japanese)
20. Yuta Yoshimoto, Yuiko Tomita1, Kohei Sato, Shiori Higashi, Masafumi Yamato, Shu Takagi, Hiroyoshi Kawakami, Ikuya Kinefuchi, Analysis of gas adsorption and diffusion processes in interfacial systems composed of a polymer of intrinsic microporosity and amorphous silica using molecular simulation techniques, 71st Polymer Symposium in Japan, September 2022 (Sapporo) (in Japanese)
21. Masafumi Yamato, Kaito Udo, Hiroyoshi Kawakami, Gas Permeability of Composite Membranes using Polymer Intrinsic Microporosity Matrix, 71st Polymer Symposium in Japan, September 2022 (Sapporo) (in Japanese)
22. Masafumi Yamato, Mizuki Akatsuka, Shiori Higashi, Hiroyoshi Kawakami, Structure and Physical Properties of Highly Loaded Films with Silica Nanoparticles, 71st Polymer Symposium in Japan, September 2022 (Sapporo) (in Japanese)
23. Takumu Morita, Masafumi Yamato, Hiroyoshi Kawakami, Particle-containing polymer membrane with high permeability for Direct Air Capture, The 71th Polymer Symposium in Japan, (Hokkaido Univ.), 3J01, Sept. 2022.
24. Takumu Morita, Masafumi Yamato, Hiroyoshi Kawakami, High permeable PIM-1 complex membrane loaded with high concentration of particles, The 71th Polymer Symposium in Japan, (Hokkaido Univ.), 3Pe065, Sept. 2022.
25. Akari Tatsukawa, Toyotaka Nakae, Hiroyoshi Kawakami, Optimization of Fabrication Process for Polymer Nanofiber Composite Membrane to Improve Proton-Exchange Membrane Properties, The 71th Polymer Symposium in Japan, (Hokkaido Univ.), 2Pa089, Sept. 2022.
26. Toyotaka Nakae, Kazuto Suzuki, Yasutaka Kuwahara, Manabu Tanaka, Hiroyoshi Kawakami, Development of Composite Polymer Electrolyte Membranes Containing Nanofibers Working in Wide Temperature Range towards Next Generation Fuel Cell, The 71th Polymer Symposium in Japan, (Hokkaido Univ.), 2L13, Sept. 2022.
27. Manabu Tanaka, Nohara Yokota, Kenta Sando, Ryodai Fujihashi, Hiroyoshi Kawakami, Lithium ion conductivity evaluation and mechanism analyses of polymer nanofiber composite electrolyte membranes, 63rd Battery Conference (Fukuoka International Conference Center), November 2022 (in Japanease)
28. Yuri Nara, Manabu Tanaka, Kensaku Nagasawa, Yoshiyuki Kuroda, Shigenori Mitsushima, Hiroyoshi Kawakami, Synthesis and Water Electrolysis Evaluation of Anion Conductive Polymers with Fluorene Backbone., The 31st Polymer Materials Forum, (Tower Hall Funabori), 1PB22, November 2022 (in Japanese)
29. Takumu Morita, Masafumi Yamato, Hiroyoshi Kawakami, Gas permeation properties of ultra-high CO2 permeable composite membranes loaded with highly concentrated surface-modified nanoparticles, Membrane Symposium 2022 in Japan, (Kobe Univ.), P-39S, Nov. 2022
30. Kota Nagano, Masafumi Yamato, and Kawakami Hiroyoshi, Effect of pressure on gas permeability of surface-modified silica nanoparticle/PIM-1 composite membranes, Membrane Symposium 2022, (Kobe University Centennial Hall), P-14S, November 2022.
31. Kazuma Komine, Masafumi Yamato, and Kawakami Hiroyoshi, Magnetic orientation of Liquid Crystal comprising Ionic Liquid and Sepiolite., 16th Magneto-Science Society of Japan , (Nihon Univ.), P-17, November 2022 (in Japanese)
32. Yusei Shinada, Masafumi Yamato, Hiroyoshi Kawakami, Orientation control of layered double hydroxides using magnetic field P-18, 2022 Annual Meeting of the Magneto-Science Society of Japan, (Online), Nov. 2022(in Japanese)
33. Yusei Shinada, Masafumi Yamato, Hiroyoshi Kawakami, Anisotropy Control of PVA/Layered Double Hydroxide (LDH) Composites P15, 95th Musashino Area Polymer Symposium, Nov. 2022(in Japanese)
34. Dong Yubing, Manabu Tanaka, Hiroyoshi Kawakami, Preparation and Lithium Ion Conductivity Evaluation of Cross-linked Network Polymer Electrolytes Containing Solvated Ionic Liquid, The 12th Ionic Liquid Symposium, Nov. 2022
35. Hidetaka Noritomi, Mariko Shimokawa, Jumpei Nishigami, Satoru Kato, Kiyoshi Sato, Hiroyoshi Kawakami, “Absorption of Enzymes on Hollow Carbon

Microparticles prepared from Lignin and Heat Stress Tolerance of Adsorbed Enzymes", SSPEJ Annual Meeting 2022, November 2022 (on line) (in Japanese)

36. Manabu Tanaka, Kazuto Suzuki, Hiroyoshi Kawakami, Proton Conductive Nanofibers-based Polymer Electrolyte Composite Membranes for Fuel Cells, MRS-J 2022 (Yokohama) December 2022
37. Momoka Chatani, Naomi Saito, Masahiro Yoshioka, Yuichi Kinoshita, Hanae Nakamura, Yuki Hashimoto, Akiko Takenouchi, Katsuhuko Yoshizawa, "Pathophysiological Inhibitory Effect of Acerola on Streptozotocin-Induced diabetic Cataract Rat Model", the 19th Annual Meeting of Society for Functional Food research (WINC AICH, hybrid), Y-4, January, 2023 (in Japanese)
38. Akiko Takenouchi, Haruna Kibi, Yukino Mori, Momoka Chatani, Hanae Nakamura, Yuki Hashimoto, Masahiro Yoshioka, Yuichi Kinoshita, Katsuhuko Yoshizawa, "Inhibitory Effects of Acerola Supplementation In Rat Model of Acute Hepatic Injury Derived from Green Tea Extract", the 19th Annual Meeting of Society for Functional Food research (WINC AICH, hybrid), G-8, January, 2023 (in Japanese)
39. Ayaka Mori, Koki MINO, Yui Okido, Keisuke Ashiba, Masahiro Yoshioka, Kiyoshi Sato, Hiroyoshi Kawakami, "Liposomal nanoparticles for maintaining cell quality", 71st Polymer Symposium in Japan, September 2022 (Sapporo) (in Japanese)
40. Dong Yubing, Manabu Tanaka, Hiroyoshi Kawakami, Synthesis and Evaluation of Polymer Gel Electrolyte Membranes Using Solvated Ionic Liquid and Their Application to Lithium Ion Batteries, The 103rd CSJ Annual Meeting, March 2023 (in Japanese)

■Patents

1. Gas separation membrane, Hiroyoshi Kawakami, Masafumi Yamato, Shiori Higashi, Takumu Morita, PCT/JP2022/030868（2022/8/15）
2. Gas separation membrane, Hiroyoshi Kawakami, Masafumi Yamato, Takumu Morita, Mizuki Akatsuka, JP2023-021451（2023/2/15）

■Awards

1. Membrane Symposium 2022 in Japan, Student Award, Takumu Morita, Masafumi Yamato, Hiroyoshi Kawakami, "Gas permeation properties of ultra-high CO2 permeable composite membranes loaded with highly concentrated surface-modified nanoparticles".
2. The 71th Polymer Symposium in Japan, Publicity Award, Takumu Morita, Masafumi Yamato, Hiroyoshi Kawakami, "Particle-containing polymer membrane with high permeability for Direct Air Capture".
3. Student Special Award, Yuri Nara, Graduate School and Faculty of Urban Environmental Sciences, Tokyo Metropolitan University

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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).

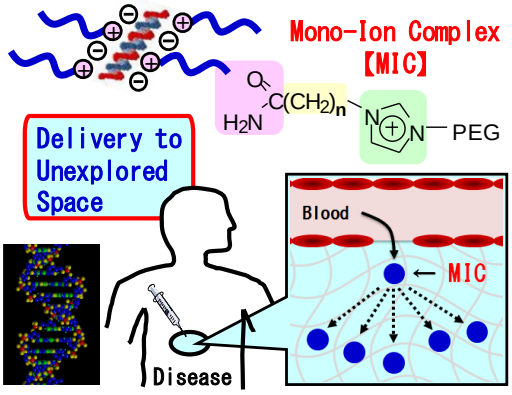

Figure 1. Delivery to *in vivo* unexplored space by the mono-ion complex (MIC).

In this year, we have synthesized 2nd generation polyamidoamine dendrimer modified with guanidinium groups, PAMAM-G2-Gu, as a pDNA carrier for floating blood cells. Especially, PAMAM-G2-Gu with a modification degree of 53 mol%, PAMAM-G2-Gu(53), showed almost no cytotoxicity. The resulting PAMAM-G2-Gu(53)/pDNA polyion complex (PIC) showed the highest gene expression ability for human leukemia cell line HL-60 among all PICs including liner carriers and branched poly(ethyleneimine) as a golden standard.

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).

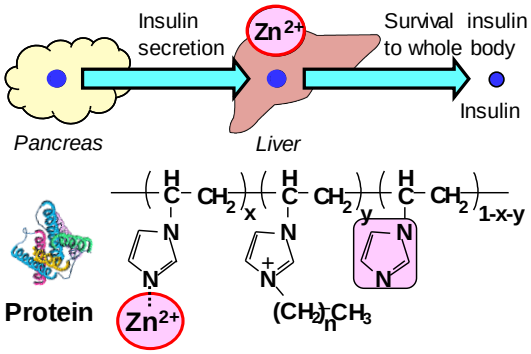

Figure 2. Remote control of hypoglycemic hormone in blood.

In this year, we have focused on the *in vivo* skeletal muscle pDNA delivery system by forming annealed pDNA/Zn^{2+}/PVIm PICs. The resulting pDNA/Zn^{2+}/PVIm PICs increased *in vitro* pDNA expression, as compared to unannealed pDNA/Zn^{2+}/PVIm PICs. Moreover, *in vivo* skeletal muscle pDNA expression mediated by the resulting annealed PICs was also greater than naked pDNA. Consequently, the annealed pDNA is considered to lead to high expression both *in vitro* and *in vivo* by retaining nonionic PVIm backbone and Zn^{2+} ions.

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).

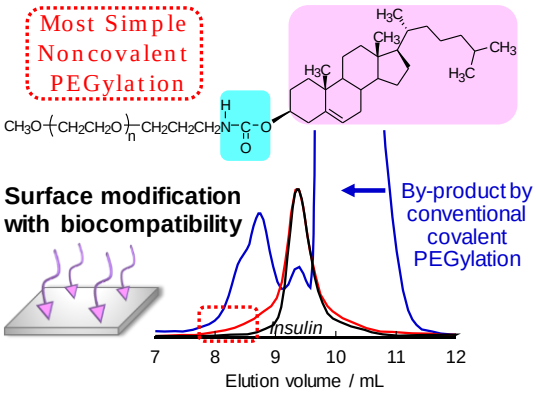

Figure 3. Development of novel bio-function by Chol-PEG.

In this year, to design more stable surface modification by increasing the ratio of a cholesterol group per molecule of Chol-PEG. Short-chain PEG (Mn=500) close to molecular weight of cholesterol anchor group was used (Chol-PEG500) for surface modification. The Chol-PEG500-coated poly(propylene) (PP) surface showed about 98% inhibition after 3-day incubation, negligible hemolysis, and inhibition of platelet adsorption. The resulting Chol-PEG500-coated PP exhibited biocompatibility comparable to long-chain PEG (Mn=2000).

■Papers with Peer Review

1. Riku Kimura, Kei Nirasawa, Yoichi Negishi and Shoichiro Asayama, Tunable gene expression in skeletal muscles by the molecular weight of PEG chain length of plasmid DNA mono-ion complexes, *Chemistry Letters*, 51, 840-843 (2022).
2. Yuki Kobayashi and Shoichiro Asayama, Design of the zinc ion and plasmid DNA co-delivery system by poly(1-vinylimidazole) derivatives for myoblast differentiation, *ACS Applied Bio Materials*, 5, 5754-5761 (2022).

■Academic Meeting

See the annual report in Japanese (13 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).

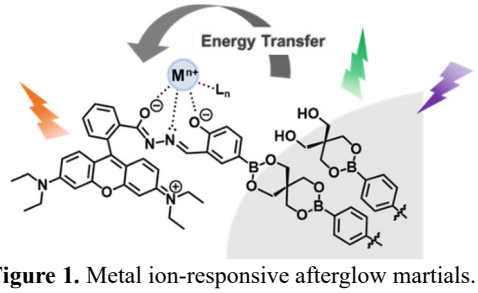

Figure 1. Metal ion-responsive afterglow martials.

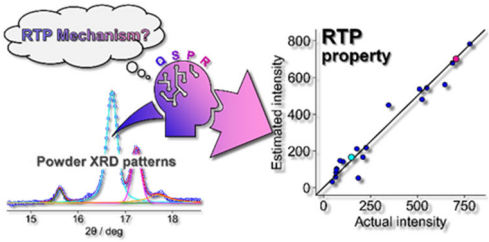

Figure 2. Chemometrics-assisted QSPR analysis.

2. Arylselanyl-BODIPYs as a sensitizer for triplet-triplet annihilation upconversion

Yuji Kubo

Abstract

Triplet-triplet annihilation upconversion (TTA-UC) has attracted increasing attention as promising method for energy conversion from low-energy excitation to higher energy light. In this study, the introduction of phenylselanide group at the 2- and 5- position of boron-dipyrromethene (BODIPY) core led to production of new triplet photosensitizer **1** (R = H), **2** (R = OMe), and **3** (R = F) The UC behavior of systems comprising the sensitizers and perylene as the acceptor in deaerated toluene was investigated using a 524 nm-wavelength laser to detect upconverted emission at 449 nm; thus, the UC yield decreased in the order of 21% for **3** > 16% for **2** > 12% for **1** (Figure 3).

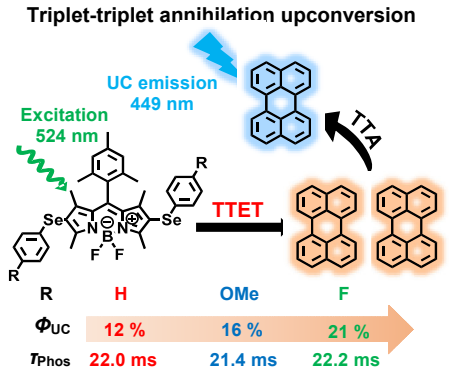

Figure 3. Arylselanyl-substituted BODIPYs as triplet sensitizers.

3. Near-infrared room-temperature phosphorescence in arylselanyl BODIPY-doped materials

Yuji Kubo

Abstract

Room-temperature phosphorescence (RTP) materials with emission bands in the NIR region are rare. Metal-free arylselanyl-BODIPY triplet photosensitizers were doped into a benzophenone (**BP**) matrix. When excited at 350 nm, RTP emission was observed in the NIR region with λ_{em} values of 750–816 nm, and the phosphorescence quantum yield was up to 0.48%. The detection of an extremely large Stokes shift

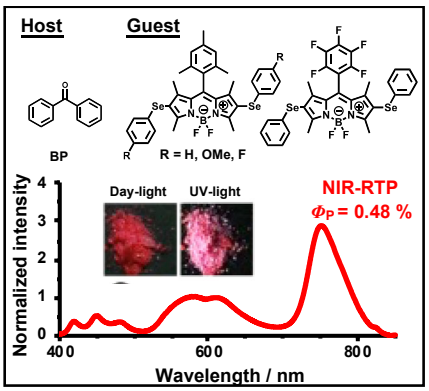

Figure 4. NIR-RTP properties of arylselanyl-substituted BODIPYs in benzophenone matrix.

(~400 nm) was responsible for the triplet-triplet energy transfer from **BP** to the BODIPY guest. Furthermore, the RTP properties were tuned by derivatization of the selenium-containing BODIPY guests. NIR-RTP properties were also detected upon excitation at 470 nm with a persistent lifetime of up to 17.5ms (Figure 4).

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.

5. Chiral recognition using quaterphenyl-5′-carbaldehyde

Yuji Kubo

Abstract

Quaterphenyl-5′-carbaldehyde **1** with metal ion coordination ability was synthesized for the first time and used for chiral analyte-binding and chiroptical sensing. The formation of an imine between **1** and amine analytes, such as alcohol amines, diamines, and amino acids, enabled Zn(II)-assisted chiral transfer from the analyte to the atropisomeric biphenyl unit, thereby amplifying the circular dichroism (CD) signal, leading to discernible Cotton effects in the range of 350–450 nm, with *g* values on the order of magnitude of 10^{-3} in MeOH. Linear relationships between the CD amplitude and enantiomer excess (ee) of the analytes were observed, enabling use of **1** as a chiroptical probe for amines. Interestingly, **1** showed a fluorescence response to change in concentrations of L-phenylalaninol in the presence of Zn(II) upon excitation at 380 nm. It suggests that **1** could serve as a dual chemosensor for the determination of both the ee and concentration of analytes (Figure 5).

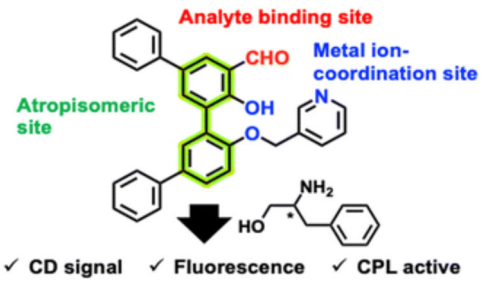

Figure 5. Chiral recognition using quaterphenyl-5′-carbaldehyde.

6. Synthesis of boron-stabilized radical with an intense emission.

Masato Ito

Abstract

We report on the fluorescence properties of a new class of emissive and stable π-radicals that contain a boron atom at a position distant from the radical center. A fully planarized derivative exhibited an intense red fluorescence with high fluorescence quantum yields even in polar solvents. To elucidate the origin of this phenomenon, we synthesized another boron-stabilized radical that contains a bulky aryl group on the boron atom. A comparison of these derivatives, as well as with conventional donor–π–acceptor (D–π–A)-type emissive π-radicals, unveiled several characteristic features in their photophysical properties. A theoretical analysis revealed that the SOMO–LUMO electronic transition generates an emissive D_1 state. Unlike conventional D–π–A-type p-radicals, this state does not undergo significant structural relaxation. The boron-stabilized π-radicals demonstrated promising potential for organic light-emitting diodes as an emitting materia (Figure 6)l.

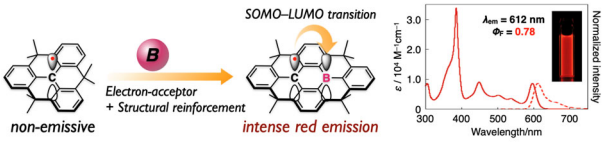

Figure 6. a) Molecular structures of a boron-stabilized radical with an intense emission.

■Papers with Peer Review

1. S. Iwakiri, R. Hasegawa and Y. Kubo, Near-infrared room-temperature phosphorescence in arylselanyl BODIPY-doped materials, *ChemPhotoChem*, **2022**, *6*, e202200073. DOI: 10.1002/cptc.202200073

2. M. Ito, S. Shirai, Y. Xie, T. Kushida, N. Ando, H. Soutome, K. J. Fujimoto, T. Yanai, K. Tabata, Y. Miyata, H. Kita and S. Yamaguchi, Fluorescent organic π-radicals stabilized with boron: Featuring a SOMO–LUMO electronic trandition, *Angew. Chem. Int. Ed.*, 2022, 134, e202201965. DOI: 10.1002/anie.202201965

3. A. Koga, K. Kawaguchi, M. C. Maida and Y. Kubo, A ratiometric afterglow response of aluminium ions in methanol-water, *Chem. Asian J.*, **2022**, *17*, e202200402. DOI: 10.1002/asia.202200402R1

4. K. Omasa, M. Ito and Y. Kubo, Zn(II)-coordination-driven chiroptical and emissive sensing for chiral amines using a quaterphenyl-5'-carbaldehyde, *New. J. Chem.*, **2022**, *46*, 21845–21851. DOI: 10.1039/D2NJ04781K

5. 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*, **2022**, *in press*. DOI: 10.1142/S1088424623500037

6. K. Kawaguchi, M. Ito and Y. Kubo, Chemometrics-assisted mechanism study of the room-temperature phosphorescence on nanoscopic boronate assemblies, *Chem. Commun.*, **2023**, *in press*. DOI: 10.1039/D2CC07049A

■Books

See the annual report in Japanese 1 book.

■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 -9
Bachelor 7

■**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.

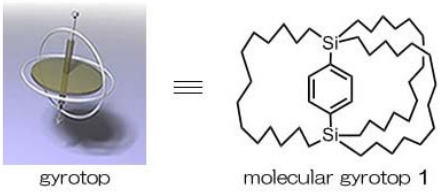

Figure 1. molecular gyrotop.

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, paper #1).

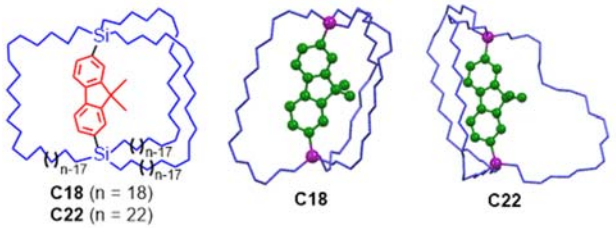

Figure 2. Fluorene-diyl bridged molecular gyrotops (paper #1).

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 with the alkyl frame. DFT calculations showed comparable stabilization from conjugation and destabilization from macroring strain. Structural differences caused changes in NMR chemical shifts and oxidation potentials. C12's properties were of interest due to its distributed structure. Overall, the findings could aid in designing functional molecules with phenylenediamine moieties (Figure 3, paper #5).

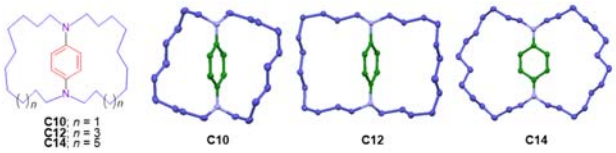

Figure 3. Phenylene-bridged diazacycloalkanes (paper #5).

Then, the development of artificial molecular rotors by novel framed molecular rotors using 1,4-naphthylene bridged diazamacrocycles were investigated. The dependence of rotation on frame size was examined, with framed rotors CnNp (n = 12, 14, 16, 18) synthesized and their rotation in solution was observed. The rotor in C18Np showed rotation, as confirmed by NMR signals, while the rotation of the naphthylene rotor in C12Np, C14Np, and C16Np was nearly suppressed in solution. The study suggests the possibility of developing functional molecular rotors using this approach (Figure 4, paper #2).

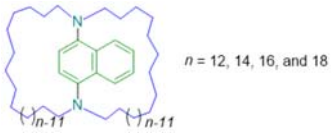

Figure 4. Naphthalene-bridged diazacycloalkanes (paper #2).

The chemistry of artificial molecular rotors has recently attracted considerable attention in the field of molecular machines. This study explores the potential of phenyltriptycene as a stepwise molecular rotor by designing the relative energies of three rotamers using CH/π-interactions between a peri-hydrogen and phenyl. Two different phenyltriptycenes were compared for CH/π-interactions, and the effects of substituents on the relative energies were investigated through various analyses. The study's findings suggest that this approach could aid in the design of molecular switches and/or rotors (Figure 5, paper #4).

Figure 5. Phenyltriptycene as a stepwise molecular rotor (paper #4).

2. Facile Synthesis of Curved π-Electron Systems

[n]Acediynes have unique properties owing to their highly strained and extended π–electron system. The article discusses the unique properties of [n]Acediynes. The synthesis of high-order silyl[n]acediynes via Eglington coupling between silyldiethynylbenzene and silyltetraethynylbenzene were investigated. The structures of silyl[1]acediyne and silyl[2]acediyne were determined using X-ray crystallography, and their spectroscopic properties were characterized with DFT calculations. A redshift in their absorption and fluorescence spectra occurred with an increase in the order number n of the [n]acediynes. The antiaromaticities of the dehydro[12]annulene moieties at the center of the annulene ring in these silylacediynes were also evaluated using NICS values. The calculated values confirmed the weak antiaromatic character of the rings (Figure 6, paper #3).

Figure 6. Structure of silyl [2]acedyine (paper #3).

■Papers with Peer Review

1. 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.*, *in press*. (DOI:10.1039/D2NJ05873A)
2. Synthesis and Rotational Dynamics of Diazamacrocycles Having Bridged 1,4-Naphthylene as Framed Molecular Rotors, T. Kurimoto, Y. Inagaki, K. Ohara, K. Yamaguchi, and W. Setaka*, *Org. Biomol. Chem.* **2022**, 20, 8465-8470. (DOI: 10.1039/D2OB01613C)
3. Synthesis and Characterization of Silyl[n]acediynes (linearly-fused benzodehydro[12]annulenes): Utilizing Bulkiness of Silyl Groups to Improve Selectivity, K. Komatsubara, Y. Inagaki, and W. Setaka*, *J. Org. Chem.* **2022**, 87, 12783-12790. (DOI:10.1021/acs.joc.2c01398)
4. Design of Rotational Potential in Phenyltriptycene Molecular Rotor by Exploiting CH/π-Interaction between Tripticil Hydrogen and Phenyl, H. Inami , Y. Inagaki, and W. Setaka*, *Org. Biomol. Chem.* **2022**, 20, 6328-6333. (DOI:10.1039/D2OB01179D)
5. Structures and Oxidation Properties of Phenylene-Bridged Diazacycloalkanes: Ring Size Effects on Structures and Properties, W. Setaka*, K. Kajiyama, and Y. Inagaki, *J. Org. Chem.* **2022**, 87, 10869-10875. (DOI:10.1021/acs.joc.2c01174)

■Invited Lectures

1. Wataru Setaka,
   Crystalline Molecular Gyrotops with a Fluorescent Rotor
   ICEAN2022, 2022.10.17-21. (Newcastle, Australia) (oral, Invited).

■Academic Meeting

＊Domestic

See the annual report in Japanese (13 articles)

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Doctor's course - 1
Master's course - 6
Bachelor 4 - 0

■**Outlines of the Research**

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

We carried out the research and development of next-generation rechargeable batteries with metals such as lithium and magnesium as anode to realize higher energy density than that of currently-used lithium-ion batteries.

The fabrication and evaluation of rechargeable lithium-metal batteries were performed as laminate-type cells. The design of practical cells with an energy density of 500 Wh kg^{-1} was successfully revealed (Fig. 1) by increasing the size and number of electrode layers gradually to 1 Ah-class, in which it was also clarified that a polyimide-polybenzimidazole mixed separator with a three-dimensional ordered porous structure (3DOM) is particularly effective on the improvement of cycleability.

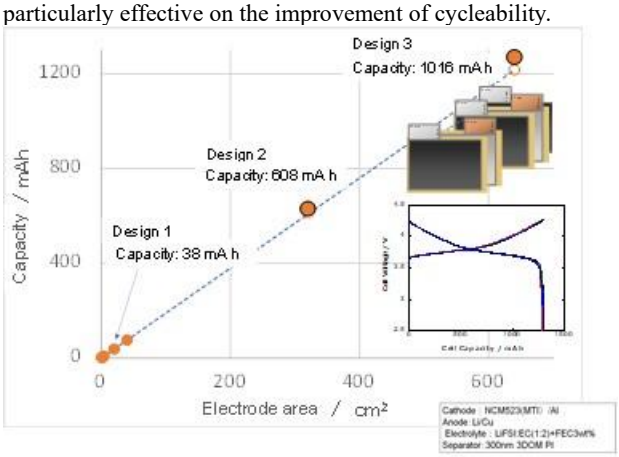

Fig. 1 The development of laminate-type rechageable lithium-metal batteries with different capacities.

We also progressed the research on rechargeable magnesium metal batteries. As one of promising cathode materials with both high operating potential and capacity, α-MnO_2 was synthesized and used in the development of laminate-type full-cells (Fig. 2). From this full cell development, we revealed a practical cell design with a prospective energy density of 300 Wh kg^{-1}. This result suggests that rechargeable batteries with an energy density exceeding that of lithium-ion batteries can be realized using magnesium as anode, which is an abundant resource. Various fundamental technologies for practical cell development such as carbon coating to suppress corrosion of Al current collector foil and separator design for magnesium metal anode were also developed, in which it was found that the optimization of electrode fabrication method is particularly important in order to improve the cell performance.

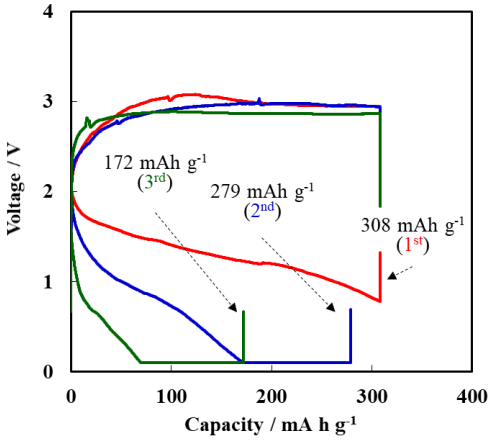

Fig. 2 Charge-discharge curves of a laminate-type rechargeable magnesium-metal battry with α-MnO_2 cathode.

2. Research on fuel cells
Kiyoshi KANAMURA, Hirokazu MUNAKATA

To improve the energy conversion efficiency of fuel cells, the operation at higher temperatures is basically needed, which enables to use waste heat more effectively in addition to the activity improvement and poisoning suppression of fuel cell catalysts. We have focused on H^+-conducting ionic liquids and their mixtures with phosphoric acid as new electrolytes usable at around 200 °C, and been developing the intermediate temperature fuel cells. However, the fuel cells using these H^+-conducting electrolytes basically require platinum-based noble metals as catalysts. Therefore, we synthesized several OH^--conducting ionic liquids and investigated them as new electrolytes to realize intermediate temperature fuel cells with non-platinum catalysts. In these OH^--conducting new electrolyte systems, oxygen reduction reaction proceeded not only on a platinum electrode but also on a glassy carbon electrode unlike in H^+-conducting electrolytes, suggesting a clear possibility of the non-platinum operation of intermediate temperature fuel cells.

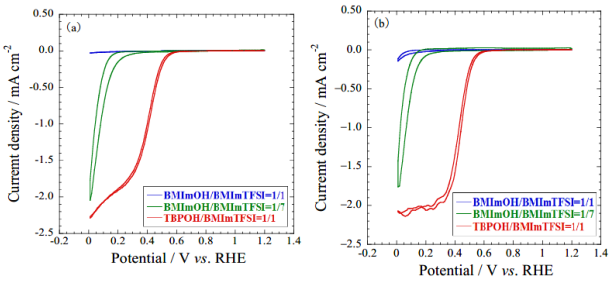

Fig. 3 Oxygen reduction reaction activity of (a) platinum and (b) glassy carbon electrodes in OH^--conducting ionic liquid electrolytes (BMImOH: 1-butyl-3-methylimidazolium hydroxide, BMImTFSI: 1-butyl-3-methylimidazolium bis(trifluoromrthanesulfonyl)imide, TBPOH: tetrabutylphosphonnium hydroxide) at 120 °C.

■**Papers with Peer Review**

1. Jik Soo Kim, Seonghyeon Lim, Rahul S. Ingole, Hirokazu Munakata, Sung-Soo Kim, Kiyoshi Kanamura, Improving the high-rate performance of LCO cathode by metal oxide coating: Evaluation using single particle measurement,

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3. Eric Jianfeng Cheng, Kei Nishikawa, Takeshi Abe, Kiyoshi Kanamura, Polymer in ceramic fexible separators for Li ion batteries, Ionics, 28 2022) 5089–5097.
4. M. Riju Khandaker, Yuki Maruyama, Masanori Nagao, Satoshi Watauchi, Hirokazu Munakata, Kiyoshi Kanamura, and Isao Tanaka, TSFZ Growth and Anisotropic Ionic Conductivity of Zr-Doped $LiCoO_2$ Single Crystals, Crystal Growth & Design, 22 (2022) 5624-5628.
5. Eric Jianfeng Cheng, Yosuke Kushida, Takeshi Abe, Kiyoshi Kanamura, Degradation Mechanism of All-Solid-State Li-Metal Batteries Studied by Electrochemical Impedance Spectroscopy, ACS Appl. Mater. Interfaces 14 (2022) 40881-40889.
6. Yueying Peng, Kei Nishikawa, Kiyoshi Kanamura, Effects of Carbonate Solvents and Lithium Salts in High-Concentration Electrolytes on Lithium Anode, Journal of The Electrochemical Society, 169 (2022) 060548.
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8. Toshihiko Mandai, Ayaka Kutsuma, Masashi Konya, Yukihiro Nakabayashi, Kiyoshi Kanamura, Room Temperature Operation of Magnesium Rechargeable Batteries with a Hydrothermally Treated $ZnMnO_3$ Defect Spinel Cathode, Electrochemistry, 90 (2022) 027005.

■Academic Meeting

＊Domestic

See the annual report in Japanese (28 articles)

＊International

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■Books and reviews

See the annual report in Japanese (5 articles)

■Awards

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Master's course -14
Bachelor 4 -8

■**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 chloroboracite $Li_4B_4Al_3O_{12}Cl$ discovered in our lab. is stable in contact with lithium. We demonstrated that this compound is usable as solid electrolytes of solid rechargeable lithium metal batteries. In this year, single crystals of $Li_4B_4Al_3O_{12}Cl$ were obtained and the structure was solved by single-crystal X-ray diffractometry (Fig. 1). The resulting structure data contribute to fundamental solid-state sciences.

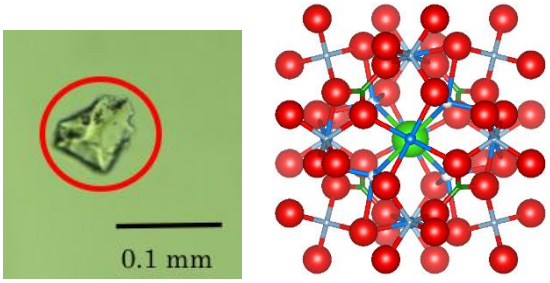


Fig. 1 A single crystal (left) and refined crystal structure (right) of $Li_4B_4Al_3O_{12}Cl$.

Silica is a ubiquitous material and its utilization is in accordance with SDGs. We are studying cosolvent-free sol-gel method to form silca-based materials only from silicon alkoxides and water without using cosolvents. The drying time of the microporous gels was successfully diminished to 30 h from 2 days, which had been the shortest record in our lab, and the yield of silica glasses was demonstrated to be as good as ~99% (Fig. 2).

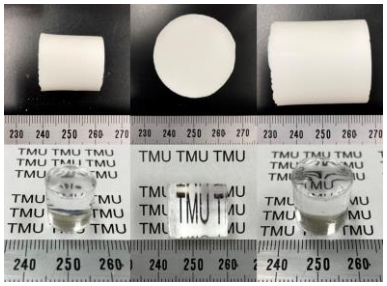


Fig. 2 Macroporous silica gels and silica glasses prepared by cosolvent-free sol–gel method.

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

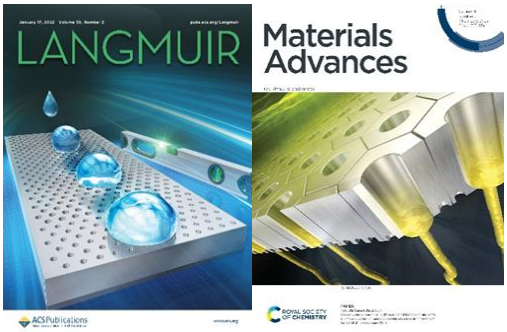
Pore size distribution is used for evaluating the basic physical properties of porous materials. The realistic pore model has been prepared by the packed silica spheres. The pore size distribution has been evaluated from the nitrogen adsorption method, thermoporometry, and mercury-intrusion-porosimetry.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

3. Fabrication of Nanofilters by Electrochemical Process
Takashi YANAGISHITA

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.

4. 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.



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2. K. Kajihara, S. Nakagawa, R. Iwasaki, Energy transfer and quenching in sol–gel-derived silica glass green phosphors doped with Tb^{3+} and Ce^{3+} ions: Distinct difference between P- and Al-codoped glasses. Phys. Status Solidi A 219, 2100494 (2022)
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4. T. Yanagishita, Y. Boushi. Preparation of anodic porous alumina with gradient hole size for directional droplet transport. Langmuir, 39, 862 (2023). [Supplementary Cover Art]
5. T. Yanagishita, K. Murakoshi, H. Masuda,Effect of fine structures formed by nanoimprinting using anodic porous alumina mold on surface hydrophobicity, ECS J. Solid State Sci. Technol., 11, 103004 (2022).
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8. T. Yanagishita, T. Sou, H. Masuda.Micro-Nano Hierarchical Pillar Array Structures Prepared on Curved Surfaces by Nanoimprinting Using Flexible Molds from Anodic Porous Alumina and Their Application to Superhydrophobic Surfaces, RSC Adv., 12, 20340 (2022).
9. T.Yanagishita.T.Masuda,H.Masuda,Pretexturing and Anodization of W for Fabricating Ordered Anodic Porous WO3. J. Electrochem. Soc., 169, 072504 (2022).
10. T. Yanagishita, R. Kawato, H. Masuda,Highly ordered anodic porous alumina prepared by anodization of Al in extremely dilute H2SO4, J. Electrochem. Soc., 169, 073504 (2022).
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See the annual report in Japanese (3 articles)

■Invited Lectures

＊Domestic

See the annual report in Japanese (6 articles)

■Academic Meeting

＊International

1. M. Ishijima, J. L. Cuya Huaman, K. Shinoda, M. Uchikoshi, H. Mamiya, J. Balachandran, Synthesis and Magnetic Properties of Co-Ni Alloy and Core-shell Structured Nanoparticle. 11th International Conference on Fine Particles Magnetism ICFPM2022, 2022/10 Yokohama, Japan Poster.
2. M. Ishijima, T. Matsumoto, J. L. Cuya Huaman, J. Balachandran, Synthesis of Transition Metals and Alloys Using Alcohol Reduction Technique, 11th International Conference on Fine Particles Magnetism ICFPM2022, 2022/10, Yokohama, Japan, Poster.

＊Domestic

See the annual report in Japanese (28 articles)

■Patents

See the annual report in Japanese (1 articles)

■Awards

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Visiting researcher 4
Doctor's course 4
Master's course 16
Bachelor 7

■**Outlines of the Research**

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

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

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

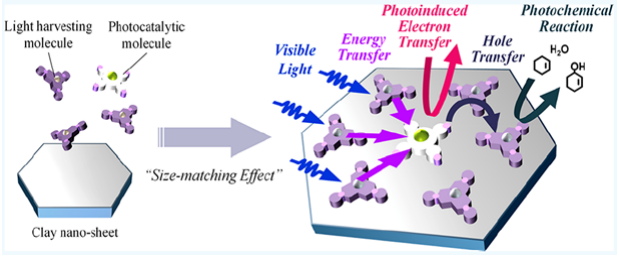

Fig. 1. Artificial light harvesting model on the nanosheet.

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

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

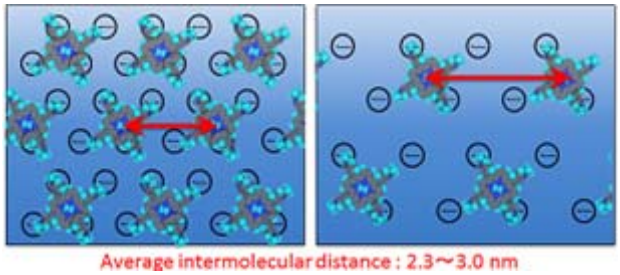

Fig. 2. An example of our methodology to control the adsorption structure of dyes on the clay surface by using a suitable clay species.

3. 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.a

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.

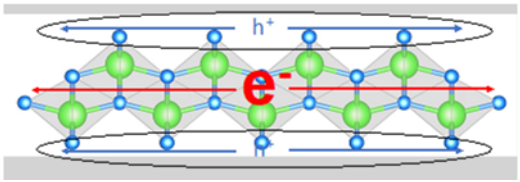

Fig. 4. Visible-light hydrogen generation reaction using the anisotropy of semiconductor nanosheets.

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. The factors that determine MQu^+-Aldehyde: MQu^+-Diol ratio were discussed from the thermodynamic analysis of the system. These data indicate that the electrostatic interaction between the charged saponite surface and MQu^+ stabilized the aldehyde side enthalpically and destabilized it entropically. The major reason for these results is considered to be the difference in adsorption stabilization between MQu^+-Aldehyde and MQu^+-Diol on saponite surfaces.

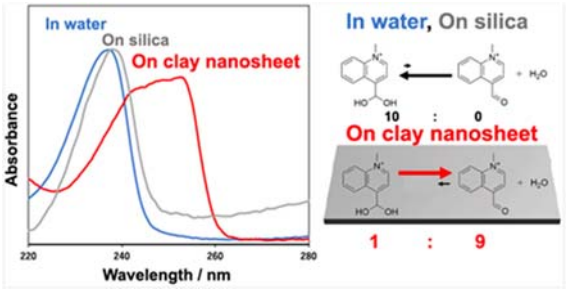

Fig. 5. The equilibrium between aldehyde (MQu^+-Aldehyde) and diol (MQu^+-Diol) in water without and with clay nanosheet.

7. Research on supported gold catalysts

Layered double hydroxides (LDHs) consist of hydroxide of divalent metal ions in which trivalent metal ions are partly substituted, and manyl kinds of LDHs are synthesized. LDH has several characteristic features: positively charged surface, intercalation of anions, converting to mixed metal oxides (MMOs) upon calcination, and exfoliating into monolayer nanosheets (NS). On the other hand, gold (Au) exhibits high catalytic activity for CO oxidation when supported as nanoparticles (NPs) of 5 nm or less in diameter on reducible metal oxides such as Co_3O_4 and NiO. However, it is difficult to support Au as small nanoparticles on inert supports such as SiO_2 and the resultant Au/SiO_2 shows low activity. In this work, we aimed at formation of active Au-oxide interface on Au NPs by the decoration of Au with thin MMO layer and evaluated the catalytic activity for CO oxidation. For this purpose, the positively charged exfoliated M-Al LDH (M: Mg, Co, Ni, and Zn) nanosheets (NS) were adsorbed on the negatively charged Au/SiO_2 to give Au/SiO_2@M-Al LDH, and then it was calcined to obtain Au/SiO_2@M-Al MMO (Fig. 6).

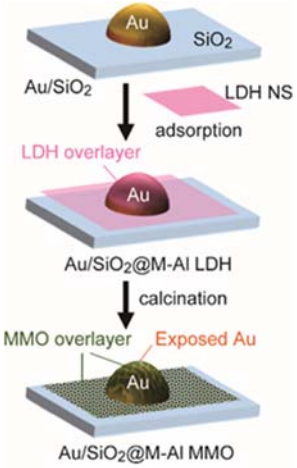

Fig. 6. Schematic image of Au/SiO_2@Co-Al MMO.

M-Al LDHs (M: Mg, Co, Ni, and Zn) were preparaed and exfoliated into monolayer NS according to the literatures. The resultant LDH NS, Au/SiO_2@M-Al LDH, and Au/SiO_2@M-Al MMO were characterized by XRD, TGA, AFM, elemental analysis, ICP-AES, TEM, HAADF-STEM, and EDX. The size of Au NPs did not change before and after the formation of MMO layer except when Mg-Al LDH was used. STEM elemental mapping of Au/SiO_2@Co-Al MMO revealed that Co and Al were highly dispersed on the whole surface of Au/SiO_2 (Fig. 7). The formation of Co-Al MMO layer on the Au NP surface was confirmed by STEM (Fig. 8).

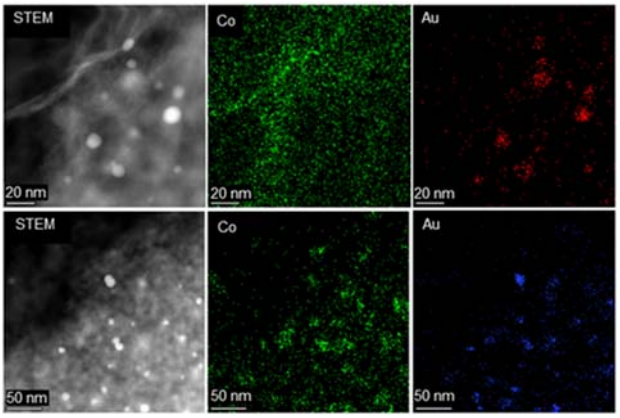

Fig. 7. STEM elemental mappings of Au/SiO_2@Co-Al MMO (upper) and of Co-Al/Au/SiO_2 (bottom).

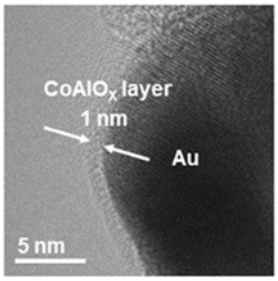

Fig. 8. TEM image of Au/SiO_2@Co-Al MMO.

■Papers with Peer Review

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6. 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(2022).
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8. Facile synthesis of Co_3O_4@SiO_2/Carbon Nanocomposite Catalysts from Rice Husk for Low-Temperature CO Oxidation, L. X. Dien, H. D. Chinh, N. K. Nga, R. Luque, S. M. Osman, L. G. Voskressensky, T. D. Lam, T. Ishida, T. Murayama, *Mol. Catal.*, **518**, 112053-112057(2022).
9. Effect of poly(N-vinylpyrrolidon) 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).

■Reviews

See the annual report in Japanese (1 articles).

■Books

1. Surface-fixation Induced Emission, Y. Ishida・S. Takagi, Wiley & Sons Ltd., "Handbook of Aggregation-Induced Emission" (Y. Tang, B. Z. Tang, Ed.), (2022).

■Invited Lectures

1. The effect of flat inorganic surface on the photochemical properties and reactions of molecules, S. Takagi, Saturday Seminar Series (Hosted By Professor V Ramamurthy), Online, March, 2022.
2. Decoration of Gold Nanoparticle Surface for Tuning the Catalytic Activity, T. Ishida, East China University of Science and Technology, Shanghai (China), December, 2022.
3. See the annual report in Japanese (2 more articles)

■Academic Meeting

＊International

1. Development of gold nanoparticle catalyst supported on Ni-Ti mixed metal oxides using layered double hydroxides, A. Takahashi, A. Nakayama, T. Murayama, N. Sakaguchi, T. Shimada, S. Takagi, T. Ishida, GOLD2022, Quebec, Canada, July, 2022.
2. Effect of strong metal-support interaction (SMSI) on gold/substituted-hydroxyapatites for oxidative esterification of aliphatic aldehydes, A. Taketoshi, Y. Gangarajula, R. Sodenaga, A. Nakayama, N. Sakaguchi, T. Murayama, M. Haruta, B. Qiao, J. Wang, T. Ishida, GOLD2022, Quebec, Canada, July, 2022.
3. Enhanced catalytic activity utilizing strong metal-support intreractions (SMSI) -Isomerization of alkenes over hydroxyapatite supported gold catalysts-, A. Nakayama, R. Sodenaga, Y. Gangrajula, A. Taketoshi, T. Murayama, T. Honma, N. Sakaguchi, T. Shimada, S. Takagi, M. Haruta, B. Qiao, J. Wang, T. Ishida, GOLD2022, Quebec, Canada, July, 2022.
4. Influence of Strong Metal-Support Interaction (SMSI) on Catalytic Properties of Substituted-Hydroxyapatite Supported Au Nanoparticles, A. Nakayama, R. Sodenaga, Y. Gangrajula, A. Taketoshi, T. Murayama, T. Honma, N. Sakaguchi, T. Shimada, S. Takagi, M. Haruta, B. Qiao, J. Wang, T. Ishida, The 9th Tokyo Conference on Advanced Catalytic Science and Technology (TOCAT9), Fukuoka, July, 2022.
5. Depositoin of gold clusters on Ni-Ti mixed metal oxide/SiO_2 having abundant oxygen vacancies and its catalytic performance for CO oxidation, A. Takahashi, A. Nakayama, T. Murayama, N. Sakaguchi, T. Shimada, S. Takagi, T. Ishida, The 9th Tokyo Conference on Advanced Catalytic Science and Technology (TOCAT9), Online (Japan), July, 2022.
6. Surface Modification of Au/SiO_2 Using Layered Double Hydroxides (LDH) and Effect on CO Oxidation, K. Okayama, A. Nakayama, T. Murayama, N. Sakaguchi, T. Shimada, S. Takagi, T. Ishida, The 9th Tokyo Conference on Advanced Catalytic Science and Technology (TOCAT9), Online (Japan), July, 2022.
7. Decoration of Au/TiO_2 surface by thin layer of metal-

organic framework and its catalytic activity, S. Kadowaki, A. Nakayama, N. Sakaguchi, T. Murayama, S. Takagi, T. Shimada, T. Ishida, The 9th Tokyo Conference on Advanced Catalytic Science and Technology (TOCAT9), Online (Japan), July, 2022.
8. Fluorescence enhancement of molecules on the clay surface and its environmental responses, S. Takagi, AIPEA - XVII International Clay Conference, Istanbul (Turkey), July, 2022.
9. Adsorption and aggregation behavior of tetracationic porphyrins on clay and titania nanosheets, Y. Hirade, K. Fukushima, T. Shimada, T. Ishida, S. Takagi, AIPEA - XVII International Clay Conference, Istanbul (Turkey), July, 2022.
10. "On surface synthesis" on saponite surface: A novel organic reaction pathway of azonia[5]helicene by interaction with saponite surface, K. Arakawa, T. Shimada, T. Ishida, S. Takagi, AIPEA - XVII International Clay Conference, Istanbul (Turkey), July, 2022.
11. Development of Suported Au Catalysts Toward the Optimization of the Electronic State of Au, A. Nakayama, The Röntgen-Angström Cluster (RÅC) International Summer School 2022 (Focal theme: Advanced Materials Design at X-ray and Neutron Facilities), Varberg (Sweden), August, 2022.
12. Effect of Covering Au Surface by Thin Layer of Hydroxyapatite on Alkene Isomerization, T. Ishida, A. Nakayama, Y. Gangarajula, A. Taketoshi, T. Murayama, T. Honma, N. Sakaguchi, T. Shimada, S. Takagi, M. Haruta, B. Qiao, J. Wang, Tateshina Conference on Organic Chemistry, Nagano (Japan), November, 2022.

＊Domestic

See the annual report in Japanese (29 articles)

■Awards

1. Excellent Presentation Award, The 47th meeting for young scientists in photochemistry, Kyosuke ARAKAWA (D1), June, 2022
2. The Clay Science Society of Japan Promotion Fund Award, The Clay Science Society of Japan, Yugo HIRADE (D2), July, 2022.
3. 2nd Best Poster Award, The Röntgen-Angström Cluster (RÅC) International Summer School 2022 (Focal theme: Advanced Materials Design at X-ray and Neutron Facilities) at Sweden, Akihiro NAKAYAMA, August, 2022.
4. Travel Awards, GOLD 2022, , Akihiro NAKAYAMA, August, 2022.
5. Excellent Poster Awards for Students, The 130th CATSJ Meetings, Shintaro KADOWAKI (M2), September, 2022.
6. Excellent presentation award, The solid and surface photochemistry conference 2022, Ryota SHIMADA (M2), November, 2022.
7. The Best Presentation Award, Symposium on Molecular Photo-Functionalities 2022, Yugo HIRADE (D2), December, 2022.

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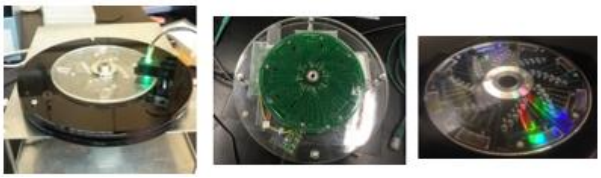
Doctor's course -4
Master's course -13
Bachelor 4 -8

■Outlines of the Research

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

Hizuru NAKAJIMA, Shoji YAMAMOTO

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



2. Development of a Portable ELISA System Using Pipette Tips

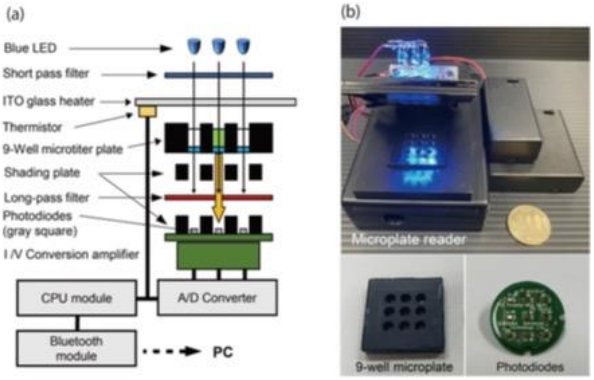
Hizuru NAKAJIMA, Shoji YAMAMOTO

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

3. Development of a Portable Genetic Testing System Based on LAMP

Hizuru NAKAJIMA, Shoji YAMAMOTO

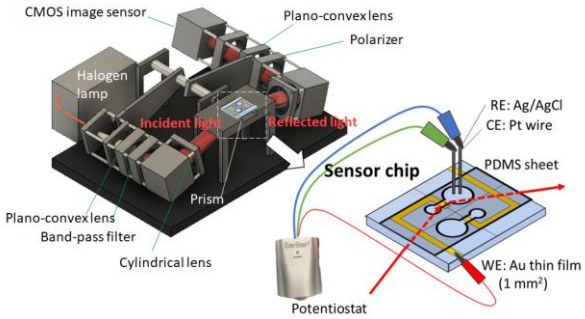
A genetic amplification method using polymerase chain reaction (PCR) is commonly used in the genetic test. However, the PCR method is not suitable for the on-site genetic test since the method needs large-sized and expensive assay devices such as a thermal cycler, an electrophoresis equipment, and an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



4. Development of Quantitative Multi-ion Channel Activity Evaluation Method Using Electrochemical Surface Plasmon Resonance sensor

Hizuru NAKAJIMA, Shoji YAMAMOTO

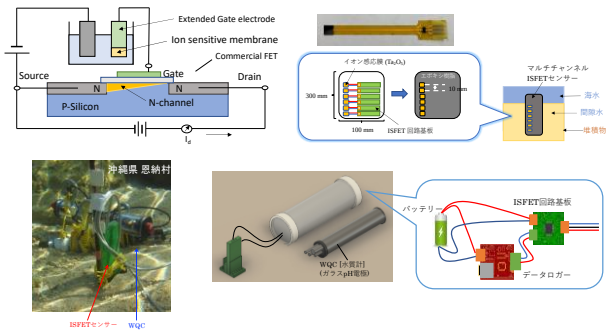
Ion channels in biological membranes are one of the targets for drug discovery, and it is important to analyze their function. The activity of ion channels is generally evaluated by electrochemical measurements, but the measurements require skilled techniques. In this study, we developed a compact multichannel electrochemical surface plasmon resonance sensor. Using our sensor, we developed a simple and quantitative method to evaluate the activity of ion channels.



5. Development of Multichannel ISFET Sensor for Measuring pH Distribution of Interstitial Water in Marine Sediment

Hizuru NAKAJIMA, Shoji YAMAMOTO

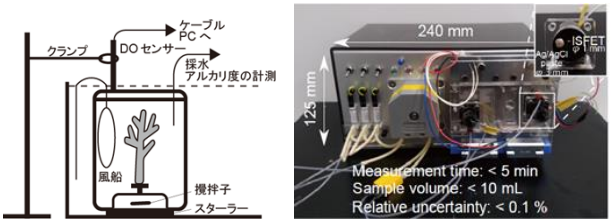
Recently, marine acidification is progressing with increasing the concentration of CO_2 in the atmosphere. Ocean acidification not only decreases the skeletal formation of calcium carbonate in corals, shellfish, and other marine organisms, but can also cause the dissolution of coral reef sands, raising concerns about the impact on marine organisms. Therefore, the measurement of the pH distribution of pore water in marine sediment is important for evaluating the effect of ocean acidification on the ecosystem. In general, the pH value of interstitial water in marine sediment is measured by divers using the pH meter with a glass electrode. However, the measurement work is very hard, the glass electrode is fragile, and the pH distribution of interstitial water could not be measured at the same time. To overcome these drawbacks, a novel multichannel ISFET sensor using Ta_2O_5 as an ion-sensitive membrane was developed for measuring the pH distribution of pore water in marine sediment.



6. Evaluation of Combined Temperature and CO_2 Stress in Corals by Continuous Measurements of Calcification and Photosynthesis

Hizuru NAKAJIMA, Shoji YAMAMOTO

Coral reef ecosystems are now facing the danger of global warming and ocean acidification due to increased CO_2 emissions. Corals that support the ecosystem are cnidarians, but they are curious organisms that obtain most of their energy to build their own skeletons (=calcification) through photosynthesis by zooxanthellae that live symbiotically within their bodies. Therefore, it is necessary to evaluate the combined stress of water temperature and CO_2 by photosynthesis of zooxanthellae and coral calcification. In this study, we successfully established a method to measure both the photosynthesis of zooxanthellae and the calcification of corals on a minute scale by measuring continuous total alkalinity and dissolved oxygen in seawater.



7. Measurements of VOCs at urban and suburban sites

Shungo KATO

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

8. 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.

9. Measurements of atmospheric pollutants at mountain sites

Shungo KATO

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

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

Shungo KATO

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

11. Hydrogen measurement in ambient aire

Shungo KATO

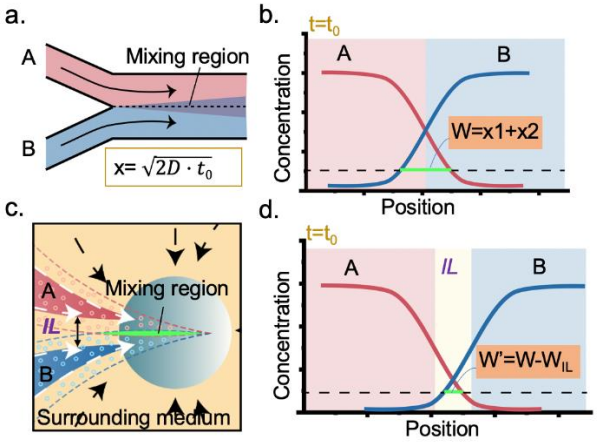
Gas chromatgrapy/Redection gas detector system was constructed for low level hydrogen measuremtns. Atmospheric hydrogen concentration in suburban, urban, and remote sites were observed. Measeruemts on tunnels to observe car exhaust were conducted.

12. Development of microchemical pen and its applications
Sifeng MAO

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

13. 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.

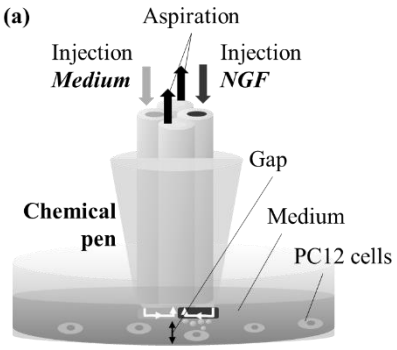


14. Regioselective fabrication of gold nanowire using open-space laminar flow for attomolar protein detection
Sifeng MAO

Gold nanowires are expected to be applied to biosensing due to their advantages, such as high stability and biocompatibility. However, it is still inconvenient to fabricate a single gold nanowire at a precise position, and without a special demanding environment. In this study, we present an open-space laminar flow approach for fabricating a single gold nanowire at a precise position under normal conditions. The fabricated gold nanowire demonstrated excellent biosensing of IgA with an extremely low limit of detection (1 aM).

15. Development of 4-nozzle chemical pen for single cell differentiation
Sifeng MAO

In this study, we developed a system using a 4-nozzle chemical pen for single cell differentiation using NGF. possible to confine the solution in the limited area in a medium. In this study, PC12 cells in the solution area were stimulated by NGF using a 4-nozzle chemical pen, and the changes in the cells were observed to examine the single cell differentiation. As a result of stimulating PC12 cells with NGF for 3 hours using this system, it was confirmed that the localization of mitochondria and lysosomes migrated to the neurites.



16. Local pH control by using a laminar flow
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.

■Papers with Peer Review

1. Yuki Nishitani, Nahoko Kasai, Hizuru Nakajima, Shungo Kato, Sifeng Mao, Katsumi Uchiyama
Regioselective fabrication of gold nanowires using open-space laminar flow for attomolar protein detection
Chemical Communications, 2022, 58(27) 4308-4311
2. Shuhui Si, Tsuguhiro Kaneko, Lingrui Xu, Huan Luo, Hizuru Nakajima, Nahoko Kasai, Katsumi Uchiyama, Danhong Wu, Hulie Zeng
Microsphere amplified fluorescence and its application in sensing
Biosensors and Bioelectronics, 2022, 218 114791-114791
3. Haifeng Lin, Nahoko Kasai, Ning Xu, Hizuru Nakajima, Shungo Kato, Hulie Zeng, Jin-Ming Lin, Sifeng Mao, Katsumi Uchiyama
Localized hydrodynamic flow confinement assisted nanowire sensor for ultrasensitive protein detection.
Biosensors and Bioelectronics, 2022, 218, 114788.
4. Masakazu Kagawa, Kazuhiro Morioka, Moeko Osashima, Akihide Hemmi, Shoji Yamamoto, Atsushi Shoji, Katsumi Uchiyama, Hizuru Nakajima
Development of small-sized fluorescence detector for pipette tip-based biosensor for on-site diagnosis
Talanta, 2023, 124311-124311
5. Sifeng Mao
Recent advances in nanowire sensor assembly using laminar flow in open space.
TRAC Trends in Analytical Chemistry, 2023, 116918.

6. Nanase Kohno, Jun Zhoua, Jiaru Li, Marina Takemur, Natsuki Ono, Yu Bai, Yasuhiro Sadanaga, Yoshihiro Nakashima, Kei Sato, Shungo Kato, Kentaro Murano, Yosuke Sakamoto and Yoshizumi Kajii
Impact of OH missing reactivity and aerosol uptake of HO2 radicals on tropospheric O3 production during the AQUAS-Kyoto summer campaign in 2018, Atmospheric Environment, 281, 119130, 2022
7. N.K. Kim, Y.P. Kim, Y.S. Ghim, M.J. Song, C.H. Kim, K.S. Jang, K.Y. Lee, H.J. Shin, J.S. Jung, Z. Wu, A. Matsuki, N. Tang, Y. Sadanaga, S. Kato, A. Natsagdorj, S. Tseren-Ochir, B. Baldorj, C.K. Song, J.Y. Lee
Spatial distribution of PM2.5 chemical components during winter at five sites in Northeast Asia: High temporal resolution measurement study
Atmospheric Environment, 290, 119359, 2022

■Invited Lectures

■Academic Meeting

＊International

＊Domestic

See the annual report in Japanese (23 articles)

■Books

■Awards

See the annual report in Japanese (1 articles)

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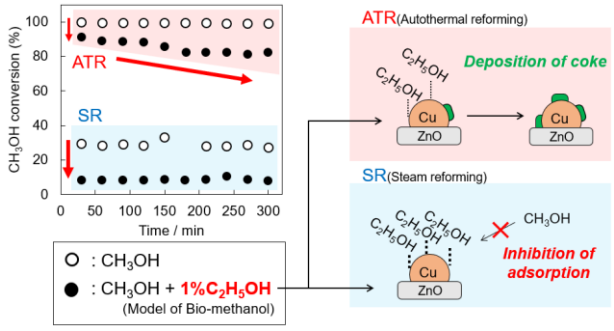
PD -1
Doctor's course -4
Master's course -10
Bachelor 4 -6

■**Outlines of the Research**

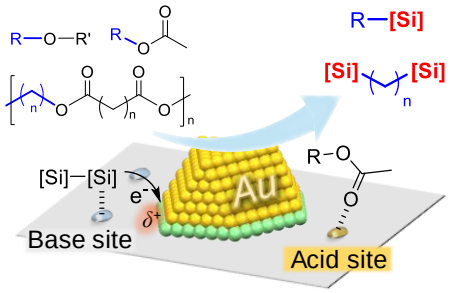
Inhibitory effect of trace impurities in biomass-derived methanol on methanol reforming by Cu-based catalysts

Steam reforming (SR) and autothermal reforming (ATR) of methanol are important reactions to produce chemicals and supply hydrogen to fuel cells. Methanol is mainly produced from fossil fuels. Therefore, utilization of biomass-derived methanol (bio-methanol) is desired from the perspective of carbon neutrality. However, the effect of impurities such as lower alcohols and aromatics in bio-methanol on methanol reforming was unclear. In this study, the effect of impurities on methanol reforming was investigated in reforming of "model bio-methanol" contained trace ethanol as model impurities. In SR, the catalytic activity of copper-zinc oxide-aluminum oxide (CZA) was remarkably decreased due to ethanol adsorption on the active site. In ATR, carbonaceous species was deposited on CZA and leaded to decrease the activity. These results suggest that Cu-based catalyst are affected by the inhibitory effect of lower alcohols due to the inability of Cu to cleave C-C bonds in lower alcohols.



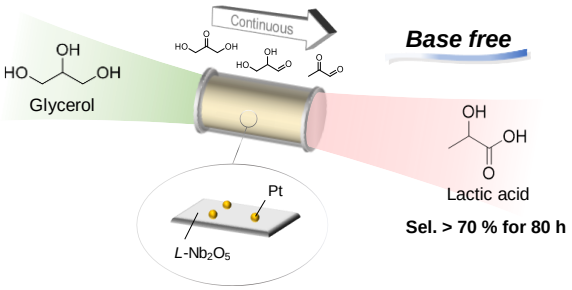
Alkyl–silyl cross-coupling with the cooperation of gold nanoparticles and amphoteric zirconium oxides

The universal transformation of C(sp^3)–O bonds will be a key technology for achieving carbon neutrality. In this study, we demostrated that gold nanoparticles supported on amphoteric metal oxides, efficiently promoted C(sp^3)–Si bond formation to give diverse organosilicon compounds. In addition, this novel reaction technology for C(sp^3)–O bond transformation could be applied to the upcycling of polyesters. Mechanistic studies corroborated the notion that the generation of alkyl radicals is involved in C(sp^3)–Si coupling and the cooperation of gold and an acid–base pair on amphoteric oxide is responsible for the homolysis of stable C(sp^3)–O bonds. The high reusability and air tolerance of the heterogeneous gold catalysts as well as a simple, scalable, and green reaction system enabled the practical synthesis of diverse organosilicon compounds.



Continuous production of lactic acid from glycerol over bifunctional catalysts using a liquid-phase flow reactor

The highly efficient conversion of glycerol into value-added chemicals with high selectivity is an attractive issue in biorefineries. In this study, the performances of metal-acid bifunctional catalysts for converting glycerol to lactic acid were investigated under an oxygen atmosphere without additives, such as strong bases using a continuous liquid-phase flow reactor. We found that Pt/*L*-Nb_2O_5 (*L*-Nb_2O_5: layered Nb_2O_5) is the most promising catalyst for the continuous production of lactic acid from glycerol due to the optimal oxidation ability and the high Lewis and Brønsted acidities of Pt/*L*-Nb_2O_5. Furthermore, Pt/*L*-Nb_2O_5 exhibited a stable catalytic performance for 80 h without a strong base.



■**Papers with Peer Review**

1. 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.
2. 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.

3. 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.
4. Transient Temperature Response of Supported Rh Nanoparticles in Photothermal Dry Reforming of MethaneAn Operando Dispersive Xray Absorption Spectroscopy Study, Takami, D.; Yamamoto, A.; Kato, K.; Shishido, T.; Yoshida, H., *J. Phys. Chem.* C, **2022**, *126*, 15736-15743.
   【Featured as a Supplementary Cover】
5. Development of ruthenium catalysts for environmentally-friendly organic transformation via C–H bond activation (*Review Paper*) Miura, H.; Shishido, T. *J. Jpn. Petrol. Inst.* **2023**, *66*, 8–14. ***【Featured as a Journal Cover】***
6. Continuous liquid-phase upgrading of glycerol to lactic acid over bifunctional catalysts under base-free conditions Kano, E.; Aihara, T.; Ghampson, I. T.; Miura, H.; Shishido, T. *ACS Sustainable Chem. Eng.* **2022**, *10*, 12072–12081.
   【Featured as a Supplementary Cover】
7. Effect of Support and Pd Cluster Size on Catalytic Methane Partial Oxidation to Dimethyl Ether Using an NO/O_2 Shuttle, Ghampson, I. T.; Yun, G-N.; Kaneko, A.; Vargheese, V.; Bando, K.; Shishido, T.; Oyama, S. T., *ACS Catal.* **2022**, *12*, 11190-11205.
8. Production of hydrogen by the autothermal reforming of methanol over Cu/ZnO/Al_2O_3-based catalysts: Improved durability and self-activation upon Pd-doping, Nomoto, K.; Kubo, Y.; Miura, H.; Shishido, T.
   J. Jpn. Petrol. Inst. **2022**, *65*, 161–170.
9. Particle Size Effect on Hydrogen Cyanide Synthesis with CH_4 and NO over an Alumina-supported Platinum Catalyst, Yamasaki, T.; Takagaki, A.; Shishido, T.; Bando, K.; Kodaira, T.; Murakami, J.; Song, J. T.; Niwa, E.; Watanabe, M.; Ishihara, T., *J. Jpn. Petrol. Inst.* **2022**, *65*, 184-191.
   【Featured as a Journal Cover】
10. Direct Air Capture of CO_2 Using Liquid Amine–Solid Carbamic Acid Phase-Separation System Kikkawa, S.; Amamoto, K.; Fujiki, Y.; Hirayama, J.; Kato, G.; Miura, H.; Shishido, T.; Yamazoe, S. *ACS Environ. Au* **2022**, *2*, 354–362.
11. Understanding the distinct effects of Ag nanoparticles and highly dispersed Ag species on N_2 selectivity in NH_3-SCO reaction Wang, H.; Murayama, T.; Lin, M.; Sakaguchi, N.; Haruta, M.; Miura, H.; Shishido, T. *ACS. Catal.* **2022**, *12*, 6108–6118.
12. Gold-Catalyzed Thioetherification of Allyl Benzyl and Propargyl Phosphates Miura, H.; Toyomasu, T.; Nishio, H.; Shishido, T. *Catal. Sci. Technol.* **2022**, *12*, 1109–1116.

■Invited Lectures

1. Novel heterogeneous organic synthesis by cooperation of gold and other elements
   H. Miura, 13th Meeting of catalysis scienece June 10, 2022 Satelite plaza Kanazawa university
2. Ag Size/Structure-Dependent Effect on Low-Temperature Selective Catalytic Oxidation of NH3 over Ag/MnO_2
   H. Wang, M. Lin, T. Murayama, M. Haruta, H. Miura, T. Shishido, Taipei International Conference on Catalysis (TICC2022) July 20-22, 2022 Taipei, Taiwan
3. Selective catalytic reduction of NO over Rh supported on hydroxyapatite
   S. Doi, H. Miura, T. Shishido, 12th International Conference on Environmental Catalysis (ICEC2022) July 30-Aug. 2, 2022 Osaka, Japan
4. Organic Transformations by Concerted Catalysis of Pd and Au on Alloy Nanoparticles
   H. Miura, JPI-KSIEC joint symposium “Advances in Material and Processing for Energy-Environmental Applications”, November 3, 2022. Daejeon, Korea.
5. Catalytic Synthesis of A-Amino Acids: Selective Conversion of Glyceric Acid to Alanine over Bifuncitional Ru/TiO_2 Catalysts
   S. Saito, H. Miura, T. Shishido, 48th Science and Technology for Advancing Toward SDGs (48th STT) Nov. 29-Dec. 1, 2022, Bangkok, Thailand
6. Basis of XAFS
   T. Shishido, 103th annual meeting of CSJ March 22—25, 2023 Tokyo university of science
7. Cooperative catalysis between gold and other elements enabling efficient organic transformation over solid surface
   H. Miura, 103th annual meeting of CSJ March 22—25, 2023 Tokyo university of science

■Academic Meeting

＊Domestic

See the annual report in Japanese (25 articles)

■Awards

1. The japan petroleum institute, The Japan Petroleum Institute Award for Distinguished Papers
   “Lactic acid production from glucose over Y_2O_3-based catalysts under base-free conditions”
   Daichi Hata, Takeshi Aihara, Hiroki Miura, Tetsuya Shishido
2. The japan petroleum institute, The Japan Petroleum Institute Award for Encouragement of Research and Development “The Japan Petroleum Institute Award for Encouragement of Research and Development”
   Hiroki Miura
3. Royal Society of Chemistry Poster Award “Low-temperature hydrogenation of CO_2 to methanol over supported gold catalysts”
   Takumi Nakagawa, Hiroki Miura, Tetsuya Shishido, The 9th Tokyo Conference on Advanced Catalytic Science and Technology (TOCAT9, Fukuoka, Virtual) July 24-29, 2022, Fukuoka, Japan
4. Presentation Award “Inhibitory effect of trace impurities on the catalytic activity in methanol reforming”
   Katsutoshi Nomoto, Hiroki Miura, Tetsuya Shishido, 12th International Conference on Environmental Catalysis (ICEC2022, Osaka, Virtual) July 30-August 2, 2022, Osaka, Japan
5. Chemical society of japan, 37th Special presentation by young researchers
   “Cooperative catalysis between gold and other elements enabling efficient organic transformation over solid surface” Hiroki Miura

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

■**Outlines of the Research**

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

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

3. Ignition control in homogeneous charge compression ignition combustion.
Internal combustion engine has higher power density and lower energy efficiency compared to fuel cell system. This research investigates a new combustion system by the compression ignition of homogeneous fuel-air mixture for achieving higher thermal efficiency in internal combustion engines. Combustion characteristics of alternative fuels such as hydrogen and ammonia in this engine system are also analyzed.

■**Papers with Peer Review**
See the annual report in Japanese

■**Academic Meeting**
＊**Domestic**
See the annual report in Japanese

■**Awards**
See the annual report in Japanese

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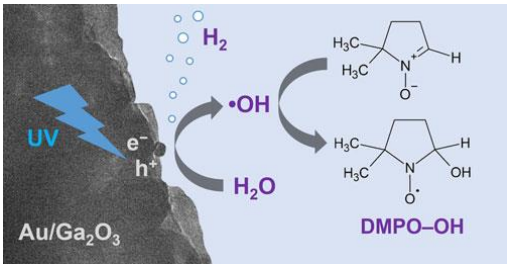
Doctor's course - 1
Master's course - 4
Bachelor (4th year) - 1

■**Outlines of the Research**

1. Photocatalytic methane conversion

We have observed that photocatalytic dehydrogenative coupling of methane ($2CH_4 \rightarrow C_2H_6 + H_2$) proceeds using Ga_2O_3-based photocatalysts under UV light irradiation in the presence of water vapor. Electron spin resonance study using DMPO as a spin-trapping agent revealed that the hydroxyl radical (•OH) concentration was high in Au/Ga_2O_3, which exhibited a high C_2H_6 production rate. The reaction mechanism accelerated by water vapor was assumed in which CH_4 was activated by •OH.

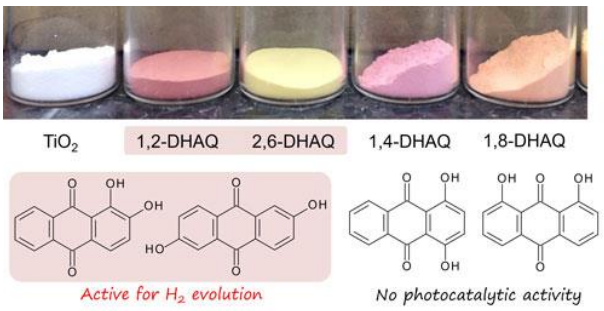


2. Electrocatalyst for water electrolysis

A mixed layer of IrO_2 and Ta_2O_5 deposited on a Ti fiber felt is an effective electrocatalyst for oxygen evolution reaction. We have studied the local structure of the amorphous IrO_2–Ta_2O_5 electrocatalysts through X-ray absorption spectroscopy. The local [IrO_6] octahedron structure in the amorphous IrO_2 nanoparticles was essential not only to achieve high activity but also high stability. During the preparation process, polyethylene glycol assisted in a complete ligand exchange from the [$IrCl_6$] octahedron to the [IrO_6] octahedron.

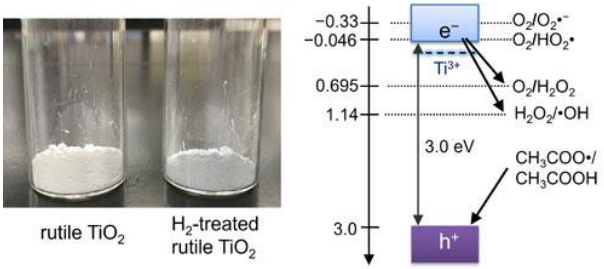
3. Dye-sensitized photocatalysts for hydrogen generation

Alizarin (1,2-DHAQ) is a stable red dye. We explored the effect of the hydroxy substituents of anthraquinone molecules on the photocatalytic H_2 evolution over a dye-sensitized Pt-TiO_2 system. The 2-hydroxy group was necessary to induce H_2 evolution under visible-light irradiation. We found that the 2-hydroxy group enhances the electron injection and suppresses the back electron transfer from TiO_2 particles to the dye.



4. Highly active rutile TiO_2 photocatalyst

Anatase TiO_2 photocatalyst can only work under UV light. Rutile TiO_2 can absorb visible light at wavelengths less than 410 nm; however, its photocatalytic activity is not high. We activated rutile TiO_2 using hydrogen reduction treatment at 700 °C. The photocatalytic activity of the H_2-treated TiO_2 was significantly higher than anatase TiO_2 under violet light irradiation at 405 nm for the oxidative decomposition of acetic acid owing to the H_2O_2 formation.



■**Papers with Peer Review**

1. F. Amano*, A. Yamamoto, J. Kumagai, Highly Active Rutile TiO_2 for Photocatalysis under Violet Light Irradiation at 405 nm, *Catalysts*, 12(10), Article 1079, 2022.
2. F. Amano*, Y. Akaki, A. Yamakata, Effects of Hydroxy Groups in Anthraquinone Dyes on Photocatalytic Activity of Visible-light-sensitized Pt-TiO_2 for Hydrogen Evolution, *Catalysis Surveys from Asia*, 27, pp 75–83, 2022.
3. F. Amano*, S. Koga, Electrochemical Impedance Spectroscopy of WO_3 Photoanodes on Different Conductive Substrates: The Interfacial Charge Transport between Semiconductor Particles and Ti Surface, *Journal of Electroanalytical Chemistry*, 921, Article 116685, 2022.
4) D.O.B. Apriandanu, S. Nomura, S. Nakayama, C. Tateishi, F. Amano*, Effect of Two-Step Annealing on Photoelectrochemical Properties of Hydrothermally Prepared Ti-Doped Fe_2O_3 Films, *Catalysis Today*, in press, 2022.
5. F. Amano*, S. Nakayama, Improvement of Water Splitting Activity of Silver-Excess $AgTaO_3$ Photocatalysts via Nitric Acid Washing Treatment, *Journal of Environmental Chemical Engineering*, 10(4), Article 108089, 2022.
6. F. Amano*, M. Ishimaru, Hydroxyl Radical Formation on Metal-Loaded Ga_2O_3 Photocatalysts for Dehydrogenative Coupling of Methane to Ethane with Water, *Energy Fuels*, 36(10), pp 5393-5402, 2022.
7. F. Amano*, Y. Furusho, S. Yamazoe, M. Yamamoto, Structure-Stability Relationship of Amorphous IrO_2-Ta_2O_5 Electrocatalysts on a Ti Felt for Oxygen Evolution in Sulfuric Acid, *The Journal of Physical Chemistry C*, 126(4), pp 1817-1827, 2022.
8. M. V. Makarova*, F. Amano*, S. Nomura, C. Tateishi, T.

Fukuma, Y. Takahashi*, Y. E. Korchev*, Direct Electrochemical Visualization of the Orthogonal Charge Separation in Anatase Nanotube Photoanodes for Water Splitting, *ACS Catalysis*, 12(2), pp 1201-1208, 2022.
9. S. Ishizuka*, J. Nishinaga, K. Beppu, T. Maeda, F. Aoyagi, T. Wada, A. Yamada, J. Chantana, T. Nishimura, T. Minemoto, M. M. Islam, T. Sakurai, N. Terada, Physical and Chemical Aspects at the Interface and in the Bulk of $CuInSe_2$-based Thin-film Photovoltaics, *Physical Chemistry Chemical Physics*, 24, pp 1262-1285, 2022.
10. R. Yoneda, K. Beppu, T. Maeda, T. Wada*, Crystallographic and Optical Properties of Wide Bandgap Photovoltaic Semiconductor System, $Cu(Al,In)Se_2$, *Japanese Journal of Applied Physics*, 61, SC1080, 2022.
11. S. Hosokawa, Y. Oshino, K. Beppu, T. Tanabe, T. Motohashi, H. Asakura, K. Teramura, T. Tanaka*, Dynamic Behavior of $Pd/Ca_2AlMnO_{5+\delta}$ for Purifying Automotive Exhaust Gases under Fluctuating Oxygen Concentration, *Catalysis Today*, in press, 2022.

■Reviews

＊Domestic

See the annual report in Japanese (1 article)

■Invited Lectures

＊International

1. Fumiaki Amano, Photocatalytic Dehydrogenative Coupling of Methane in the Presence of Water Vapor, *Post Symposium of TOCAT9, 60th Aurora seminar, The 9th International Symposium of Institute for Catalysis*, August 1, 2022, Hokkaido University, Institute for Catalysis

＊Domestic

See the annual report in Japanese (3 lectures)

■Academic Meeting

＊International

1. Fumiaki Amano, Vapor-fed photoelectrochemical water splitting by gas diffusion photoelectrodes, *The 9th Tokyo Conference on Advanced Catalytic Science and Technology (TOCAT9)*, July 25, 2022, Fukuoka International Congress Center, Oral presentation
2. Satoshi Nakayama, Fumiaki Amano, Improvement of Photocatalytic Activity of Ag-excess $AgTaO_3$ via HNO_3 Treatment, *TOCAT9*, July 25, 2022, Fukuoka International Congress Center, Short presentation, Poster presentation
3. Fumiaki Amano, Gas-Phase Photoelectrochemical Reactions using WO_3 Photoanode Decorated with Tungsto(VI) Phosphoric Acid, *The 73rd Annual Meeting of the International Society of Electrochemistry (ISE)*, September 13, 2022, Online, Oral presentation
4. Dewangga Oky Bagus Apriandanu, Shinpei Nomura, Satoshi Nakayama, Kento Shibata, Fumiaki Amano, Fe_2O_3 Photoanodes on Different Conductive Substrates for Photoelectrochemical Oxygen Evolution Reaction, *The 73rd Annual Meeting of the ISE*, September 13, 2022, Online, Oral presentationc

＊Domestic

See the annual report in Japanese (11 presentations)

Applied Chemistry Colloquium

397rd 2022/8/10

Hiroyuki Isobe (Department of Applied Chemistry, The University of Tokyo)

" A versatile synthetic method for nanocarbon molecules: The first step"

398th 2022/10/5

Kazuya Yamaguchi (Department of Applied Chemistry, School of Engineering, The University of Tokyo)

" Development of Environmentally Friendly Dehydrogenative Oxidation Reactions Using Multi-Functional Heterogeneous Catalysts"

399th 2022/11/25

Junya Ohyama (Faculty of Advanced Science and Technology, Kumamoto University)

" Study on structure effect on supported metal catalysts by atomic-scale analysis and machine learning"

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