TOKYO
METROPOLITAN
UNIVERSITY

Faculty of Environmental Sciences
Division of Applied Chemistry

Graduate School of Environmental Sciences
Department of Applied Chemistry

Annual Report 2017

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■**Outlines of the Research**

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

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

In this year, we focused on new types of nanoparticles, including pearl-necklace shaped and chain shaped silica nanoparticles that have originally inter-connected structures (Figure 1). As a result, we achieved to demonstrate extremely high CO_2 permeability by using the composite membrane containing surface-modified pearl-necklace shaped silica nanoparticles. Furthermore, the mechanism for the improvement of CO_2 permeability in these composite membranes was analyzed by utilizing the ^{13}C-NMR spectroscopy with $^{13}CO_2$ probe and gas adsorption measurements.

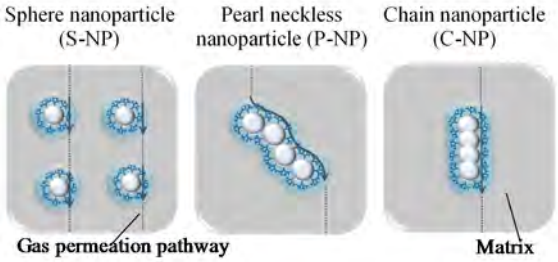

Figure 1. Schematic illustration of the polymer composite membranes containing the surface-modified silica nanoparticles with various shapes.

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

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 fabricated novel electrospun polymer nanofibers containing sulfonate and phosphonate groups that can form effective proton conductive pathway inside the nanofibers (Figure 2). The novel polymer composite membranes composed of the blend or core/shell nanofibers showed higher proton conductivity than the conventional composite membranes, especially under low humidity conditions, which are assumed as future fuel cell operation conditions.

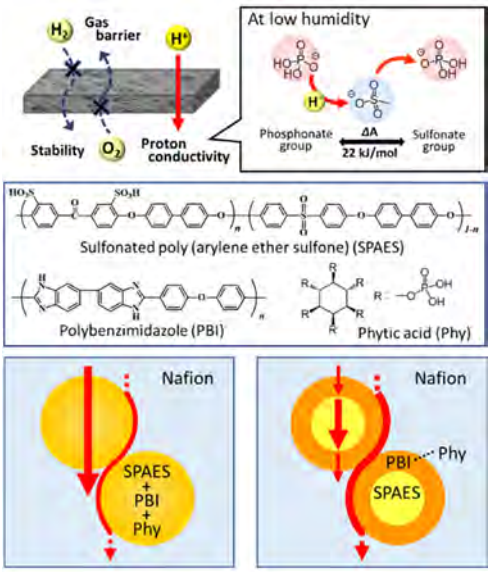

Figure 2. Schematic illustration of the novel polymer electrolyte composite membranes based on the blend or core/shell nanofibers.

3. Study of Electrospun Nanofibers
Hiroyoshi KAWAKAMI, Manabu TANAKA, Manjit Singh GREWAL

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 mainly focused on the fabrication of lithium ion conductive polymer nanofibers and their composite membranes for the secondary battery applications (Figure 3). The novel lithium ion conductive nanofiber composite membranes showed higher lithium ion conductivity than the corresponding membranes without the nanofibers, especially at low temperatures. All solid state lithium ion batteries, including a multi-stacked bipolar type, using the nanofiber composite membranes were fabricated and evaluated.

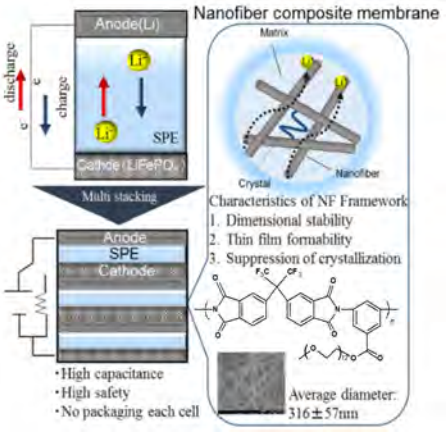

Figure 3. Schematic illustration of the lithium ion battery using the lithium ion conductive polymer nanofiber composite membrane.

4. Supramolecular system for multi-electron redox catalyst
Hiroyoshi KAWAKAMI, Riku KUBOTA,
Fidelis SIMANJUNTAK

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

In this year, we have prepared novel supramolecular system composed of dinuclear metalloporphyrin and Cucurbit[10]uril (CB[10]) for multi-electron catalysis. The resulting supramolecular system electrochemically produced hydrogen under weakly acidic conditions, Furthermore, the supramolecular system produced hydrogen from glucose as a model of hydrogen carrier.

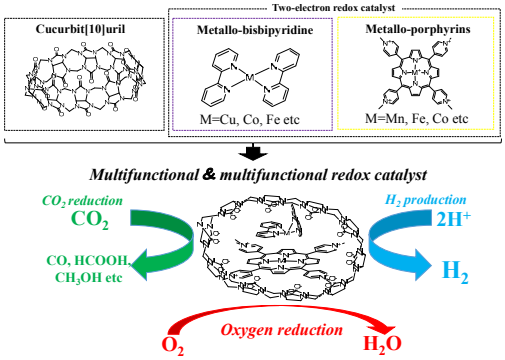

Figure 4. Multi-electron redox reactions by supramolecular bimetallic complex.

5. Study of Epigenetics Engineering
Hiroyoshi KAWAKAMI, Shoichiro ASAYAMA,
Riku KUBOTA

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

In this year, we have prepared novel epigenetics control carrier (EpC) containing single chain lipid. The resulting EpC carrier exhibited long-term stability. On the other hand, interestingly, the physicochemical properties of the EpC carrier was dependent on pH. These advantages have lead to an ability to control gene expression of the EpC carrier. Therefore, the novel EpC carrier may be useful to re-activate the inactivated gene expression which is involved in pathogenesis of severe diseases.

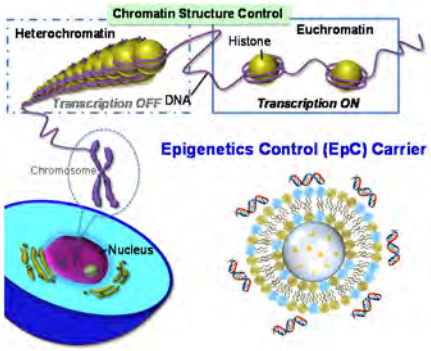

Figure 5. Gene expression control by the epigenetics control (EpC) carrier.

6. Study of Free Radical Control by Artificial Enzyme
Hiroyoshi KAWAKAMI, Shoichiro ASAYAMA,
Riku KUBOTA

Superoxide dismutase (SOD) or catalase (CAT) are well known to efficiently eliminate superoxide radicals or hydrogen peroxide as the most important antioxidants. We demonstrated that a water-soluble cationic Mn-porphyrin with SOD activity or catalase activity exhibited anticancer activity as well as antioxidative activity.

In this year, we have prepared novel biodegradable nanoparticle having capacity of gene expression and antioxidation (MnPD). The efficiency for intracellular localization of MnPD was enhanced by EpC carrier. Furthermore, the EpC carrier exhibited significant anti-inflammatory effect in Chronic Obstructive Pulmonary Disease (COPD) model *in vitro*.

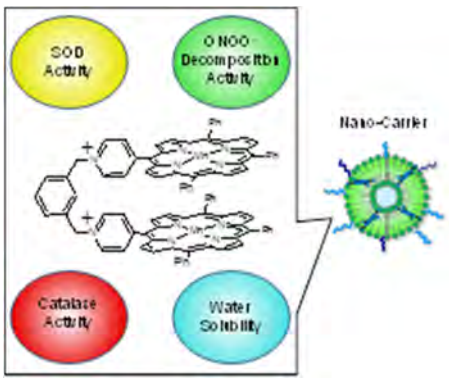

Figure 6. Mn-porphyrin (MnP) with anitioxidative activity and MnP nano-carrier.

7. Materials for Drug Delivery System

Shoichiro ASAYAMA, Hiroyoshi KAWAKAMI

To improve human health and quality of life (QOL), we have designed new biomaterials for drug delivery system (DDS). The resulting carriers for DDS such as nucleic acid (pDNA, siRNA), protein, and Zn^{2+} are expected to satisfy unmet medical needs.

In this year, to improve our original mono-ion complex (MIC : Figure 7), we have designed the *in vivo* gene delivery system for sustainable expression by biodegradable MIC. By use of the resulting MIC, diffusive and sustainable gene expression after 2 week post-injection was achieved. Furthermore, we have established the high-density modification of biomaterial surface with cholesterol end-modified poly(ethylene glycol). The nonspecific interaction of proteins with the resulting poly(propylene) surface was suppressed.

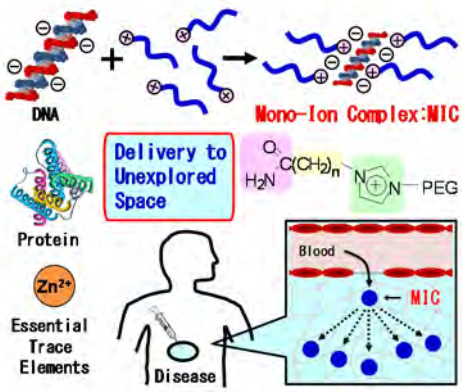

Figure 7. Delivery to *in vivo* unexplored space by the mono-ion complex (MIC).

8. 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.

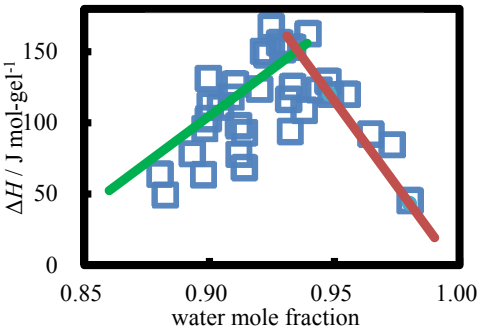

Figure 8. Water fraction dependence of enthalpy of coil-globule transition

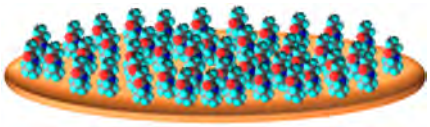

Figure 9. Schematic drawing of NIPAm molecules adsorbed on clay.

The following was examined in this year. Mixing different clay types made it possible to create a hybrid gel with anisotropy. In addition, we estimated the amount of molecules adsorbed on clay from the water fraction dependence of the enthalpy of coil - globule transition and clarified high density adsorption of molecules on the clay surface. When combined with the result of birefringence of the hybrid gel prepared in the magnetic field, it was suggested that the molecules are anisotropically adsorbed by hydrophobic interaction on the clay surface.

■Papers with Peer Review

1. Genki Ito, Manabu Tanaka, Hiroyoshi Kawakami, “Sulfonated polyimide nanofiber framework: Evaluation of intrinsic proton conductivity and application to composite membranes for fuel cells”, *Solid State Ionics* (2018) in press.

2. Shoichiro Asayama, Kana Nagashima, Yoichi Negishi, Hiroyoshi Kawakami, “By-product-free intact mofdification of insulin by cholesterol end-modified poly(ethylene glycol) for in vivo protein delivery”, *Bioconjugate Chemistry*, 29, 67-73 (2018).

3. Masanari Nakayama, Satoshi Kajiyama, Akihito Kumamoto, Tatsuya Nishimura, Yuichi Ikuhara, Masafumi Yamato, Takashi Kato, “Stimuli-responsive hydroxyapatite liquid crystal with macroscopically controllable ordering and magneto-optical functions”, *Nature Communications*, **9**, 568.1-9 (2018).

4. Shoichi Hasebe, Satoshi Aoyama, Manabu Tanaka, Hiroyoshi Kawakami, "CO2 separation of polymer membranes containing silica nanoparticles with gas permeable nano-space", *Journal of Membrane Science*, **536**, 148-155 (2017).

5. Manabu Tanaka, Yasushi Takeda, Takeru Wakiya, Yuta Wakamoto, Kaori Harigaya, Tatsunori Ito, Takashi Tarao, Hiroyoshi Kawakami, "Acid-doped polymer nanofiber framework: Three-dimensional proton conductive network for high-performance fuel cells", *Journal of Power Sources*, **342**, 125-134 (2017).

6. Takahito Makinouchi, Manabu Tanaka, Hiroyoshi Kawakami “Improvement in characteristics of a Nafion membrane by proton conductive nanofibers for fuel cell applications”, *Journal of Membrane Science*, **530**, 65–72 (2017).

7. Tsukasa Watanabe, Manabu Tanaka, Hiroyoshi Kawakami, “Anion Conductive Polymer Nanofiber Composite Membrane: Effects of Nanofibers on Polymer Electrolyte Characteristics”, *Polymer International*, **66**, 382-387 (2017).

8. Motoyuki Matsuho, Riku Kubota, Shoichiro Asayama, Hiroyoshi Kawakami, “Lactoferrin-modified nanoparticles loaded with potent antioxidant Mn-porphyrins exhibit enhanced antioxidative activity in vitro intranasal brain delivery model”, *Journal of Materials Chemistry B*, **5**, 1765-1771 (2017).

9. Shoichiro Asayama, Kana Nagashima, Hiroyoshi Kawakami, “Facile method of protein PEGylation by a mono-ion complex”, *ACS Omega*, 2, 2382-2386 (2017).

10. Shoichiro Asayama, Mizuki Sakata, Hiroyoshi Kawakami, “Structure-activity relationship between Zn^{2+}-chelated poly(1-vinylimidazole) and gene transfection”, *Journal of Inorganic Biochemistry*, 173, 120-125 (2017).

■Books

1. Shoichiro Asayama, Leading biomaterials, Journal for Japanese Society of Biomaterials, 36, 10 (2018).

2. Shoichiro Asayama, See the annual report in Japanese (2017).

3. Masafumi Yamato, Kohki Takahashi, Kazuo Watanabe,

Study in interacton between organic molecules and clay using magnetic alignment, 2016 Annual report of high field laboratory for superconducting materials in institute for materials research at Tohoku university, p.p. 143-144 (2017) (in Japanese)
4. Atsushi Mori, Masafumi Yamato, Kohki Takahashi, Structural anisotropy in silica gels prepared in magnetic field from viewpoint of alignment transition, 2016 Annual report of high field laboratory for superconducting materials in institute for materials research at Tohoku university, p.p.137-138 (2017) (in Japanese)
5. Manabu Tanaka, Gas separation using polymer membranes, Chemistry & Education, 65, 630-631 (2017) (in Japanaese)

■Invited Lectures

1. Shoichiro Asayama, See the annual report in Japanese (2017).
2. Manabu Tanaka, Tsukasa Watanabe, Hiroyoshi Kawakami, Ion Conductive Polymer Nanofiber Framework for All-Solid-State Lithium Ion Battery, The 21st International Conference on Solid-State Ionics(SSI-21), Padova, Italy (June, 2017)
3. Manabu Tanaka, Hiroyoshi Kawakami, Polymer Composite Membranes based on Proton Conductive Nanofiber Framework for Fuel Cell Applications The 17th IUPAC International Symposium on MacroMolecular Complexes (MMC-17), Waseda University (June, 2017)
4. Manabu Tanaka, Fuel cell and battery applications of ion conductive nanofibers, TIRI Cross meeting 2017 (June, 2017) (in Japanese)
5. Shoichiro Asayama, Plasmid DNA delivery system based on Zn^{2+} ions for up-regulation of gene expression, The 3rd International Forum on Applied Chemistry (September, 2017)
6. Masafumi Yamato, Thermal and magnetic properties of polymer, 2017 Basic seminar of polymer science for young engineers, Oct. 2017, Hiratsuka, Japan (in Japanese)
7. Manabu Tanaka, Ion Conductive Polymer Nanofiber Framework: Fabrication, Characterization and Application to Polymer Electrolyte Fuel Cells, The 2nd International Symposium on Hydrogen Energy–based Society, Research Center for Hydrogen Energy-based Society, Tokyo Metropolitan University (November 2017)
8. Masafumi Yamato, Higher order structure analysis for polymeric materials, Seminar of equipment analysis for polymers, Dec. 2017, Tokyo, Japan (in Japanese).
9. Hiroyoshi Kawakami, Fuel cell application of polymer electrolyte membrane composed of proton conductive nanofiber, The Electrochemical Society of Japan, Tokyo (April 2017) .
10. Hiroyoshi Kawakami, Novel all splidpolymer electrolyte membranes composed of ion conductive nanofibers, The Membrane Society of Japan, Tokyo (May 2017) .
11. Hiroyoshi Kawakami, Chemistry saves the earth, The 1st Advanced Research Forum, Tokyo Metropolitan University (June 2017) .
12. Hiroyoshi Kawakami, Ultra-high CO_2 separation membrane with nao-space, JTIC (Tokyo) , (August 2017) .
13. Hiroyoshi Kawakami, Innovative CO_2 separation membrane with nao-space, The society of polymer science of Japan (Tokyo) , (March 2018) .
14. Hiroyoshi Kawakami, Big Ideas In Chemistry, Waseda University (Tokyo) , (March 2018) .

■Academic Meeting

1. Shoichiro Asayama, See the annual report in Japanese (2017).
2. Manabu Tanaka, Yuki Kudo, Masafumi Yamato, Hiroyoshi Kawakami, Analysis on the gas permeation mechanism of PIM-1 composite membranes containing surface-modified silica nanoparticles, 39th Annual Meeting on The Membrane Society of Japan, Waseda University, 1B-02 (May 2017) (in Japanese)
3. Yuta Inafune, Manabu Tanaka, Hiroyoshi Kawakami, Fabrication and evaluation of bipolar stacked all-solid-state secondary battery with lithium ion conductive nanofiber composite electrolyte membranes, 39th Annual Meeting on The Membrane Society of Japan, Waseda University, P-38S (May 2017)
4. Takahiro Ogura, Manabu Tanaka, and Hiroyoshi Kawakami, Fabrication and fuel cell characterizations of acid-doped nanofiber composite membranes bearing the connective proton conductive pathways, The 39th annual meeting of Japanese society for membrane,(Waseda university), P-35S (May, 2017) (in Japanese)
5. Risa Sakaguchi, Manabu Tanaka, Hiroyoshi Kawakami, Fuel cell characterization of acid/base blend polymer nanofiber composite membranes, 39th The Membrane Society of Japan, (Waseda University), (May. 2017) (in Japanese)
6. Hiroto Mikami, Yuri Kameyama, Manabu Tanaka, Masafumi Yamato, Hiroyoshi kawakami, Analysis of the CO2 permeation mechanism of polyimide composite containing mixture silica nanoparticles with different morphologies, Symposium of Membranes, Waseda university, Japan, P-13S (May, 2017) (in Japanese)
7. Shun Nakazawa, Manabu Tanaka, Hiroyoshi Kawakami, Preparation and secondary battery characterizations of lithium single-ion conducting nanofiber composite membrane., 39th Annual Meeting on The Membrane Society of Japan, Waseda University, P-37S (May 2017)
8. Shoichiro Asayama et al., See the annual report in Japanese (2017).
9. Shoichiro Asayama et al., See the annual report in Japanese (2017).
10. Ryosuke Shinohara, Riku Kubota, Shoichiro Asayama and Hiroyoshi Kawakami, Preparation of alkyl amine coating biodegradable nanocarrier with epigenetics controlling ability, 66th SPSJ Annual Meeting(Makuhari Messe) (May, 2017)
11. Yuma Yokokawa, Riku Kubota, Shoichiro Asayama, Hiroyoshi Kawakami, Inhibition of Aβ aggregation by β-CD-modified anionic polymer, Polymer Preprints, Japan, Vol.66, (Makuhari messe)2Pe101 (May, 2017) (in Japanese)
12. Yuri Kameyama, Yuki Kudo, Manabu Tanaka, and Hiroyoshi Kawakami, Gas permeation property of polymer composite membranes containing silica nanoparticles having connected structures., 66th SPSJ Annual Meeting, Japan, (Makuhari Messe), 1Pb082 (May 2017) (in Japanese)
13. Riku KUBOTA, Taiga TAKABE, Hideaki TANIGUCHI, Hiroyoshi KAWAKAMI, Catalytic activity of novel water-soluble supramolecular system bearing four-electron redox properties, The 66th SPSJ Annual Meeting(Makuhari Messe), May 2017.
14. Yuta Inafune, Manabu Tanaka, Hiroyoshi Kawakami, Preparation of bipolar stacked all-solid-state secondary battery by lithium ion conductive nanofiber composite electrolyte membrane, 66th Annual meeting of society of polymer science of Japan (Makuhari Messe), 1Pe079 (May 2017)
15. Yuta Inafune, Tsukasa Watanabe, Manabu Tanaka, Hiroyoshi Kawakami, Evaluation of all-solid-state secondary battery using lithium conductive nanofiber composite electrolyte membrane, 66th Annual meeting of society of polymer science of Japan (Makuhari Messe), 3G05 (May 2017)
16. Kohe Arima, Riku Kumota, Shoichiro Asayama and

Hiroyoshi Kawakami, Curative effect of liposome-coated nanoparticle having antioxidant activity / gene expression capacity on oxidative stress disease, 65th SPSJ Annual Meeting, Makuhari, Japan (May, 2017)

17. Takahiro Ogura, Manabu Tanaka, and Hiroyoshi Kawakami, Fabrication and fuel cell characterizations of acid-doped nanofiber composite membranes bearing the connective proton conductive pathways, 66th SPSJ Annual Meeting(Makuhari Messe), 1Pf088(May, 2017) (in Japanese)

18. Takahiro Ogura, Takahito Makinouchi, Manabu Tanaka, and Hiroyoshi Kawakami, Fuel cell characteristics of acid-doped nanofiber composite membranes consisted of densified/multi-layer surface-modified nanofiber frameworks, 66th SPSJ Annual Meeting(Makuhari Messe), 3G12(May, 2017) (in Japanese)

19. Eiko Ito, Yuki Kudo, Manabu Tanaka, Masafumi Yamato, Hiroyoshi Kawakami, Analysis of nano-space in composite membranes containing nanoparticles., 65th SPSJ Annual Meeting, Japan(Makuhari Messe), 1P081 (May 2017) (in Japanese)

20. Masafumi Yamato, Shoma Mochizuki, Kotaro Oyama, Hiroyoshi Kawakami, and Noriyuki Hirota, Development of mixed-clay hybrid gel and its mechanical property, 66th SPSJ Annual meating, Makuhari Messe, (2Pb046) (May, 2017) (in Japanese)

21. Takabe Taiga, Taniguchi Hideaki, Kubota Riku, Kawakami Hiroyoshi, Functional evaluation of novel water-soluble supramolecular system with multi-electron oxidation-reduction capability, The 66th Symposium on Macromolecules (Makuhari Messe), 1Pc091 (May, 2017) (in Japanese)

22. Risa Sakaguchi, Manabu Tanaka, Hiroyoshi Kawakami, Preparation and fuel cell characterization of acid/base blend polymer nanofiber composite membranes, SPSJ Annual Meeting, (Makuhari Messe), (May. 2017) (in Japanese)

23. Hiroto Mikami, Yuki Kudo, Manabu Tanaka, Masafumi yamato, Hiroyoshi kawakami, Analysis on the gas permeation mechanism of high gas permeable composite membranes containing surface-modified silica nanoparticles, 66th SPSJ Annual Meeting , Makuhari Messe, Japan, 2F10 (May, 2017) (in Japanese)

24. Hiroto Mikami, Yuri Kameyama, Manabu Tanaka, Hiroyoshi kawakami, Analysis of the CO2 permeation mechanism of polyimide composite containing mixed silica nanoparticles with different morphologies, 66th SPSJ Annual Meeting, Makuhari Messe, Japan, 1Pa083 (May, 2017) (in Japanese)

25. Shun Nakazawa, Manabu Tanaka, Hiroyoshi Kawakami, Nanofiber fabrication and electrolyte characterizations of lithium single-ion conducting polymers bearing bis(sulfonyl)imide anion side groups, 66th Annual meeting of society of polymer science of Japan (Makuhari Messe), 1Pe080 (May 2017)

26. Shun Nakazawa, Tsukasa Watanabe, Manabu Tanaka, Hiroyoshi Kawakami, Preparation and conductive characteristics of lithium single-ion conducting nanofiber composite membranes, 66th Annual meeting of society of polymer science of Japan (Makuhari Messe), 3G06 (May 2017)

27. Yushi Minami, Riku Kubota, Shoichiro Asayama, Hiroyoshi Kawakami, "$ONOO^-$ disproportionation of novel water-soluble supramolecular system composed of Mn-porphyrin/bipyridine derivative /cucurbit[10], 66th SPSJ Annual Meeting,(May,2017),(in Japanese)

28. Kosuke Chikuma, Misaki Ouchi, Kazuhiko Nakabayashi, Riku Kubota, Shoichiro Asayama, Hiroyoshi Kwakami, Intranuclear behavior and chromatin structural regulation of cyclodextrin-modified anionic polymer, 66th Annual meeting of society of polymer science of Japan, 1Pe109, May 2017, Chiba, Japan (in Japanese)

29. Yuta Inafune, Manabu Tanaka, Hiroyoshi Kawakami, Fabrication and evaluation of multi stacked all-solid-state secondary battery comprising of lithium conductive nanofiber composite electrolyte membranes, The Annual Meeting of the Society of Fiber Science and Technology, Japan(Tower Hall Funabori), 2P213 (June 2017)

30. Yuta Inafune, Tsukasa Watanabe, Manabu Tanaka, Hiroyoshi Kawakami, Fabrication and evaluation of all-solid-state secondary battery using lithium ion conductive nanofiber framework, The Annual Meeting of the Society of Fiber Science and Technology, Japan(Tower Hall Funabori), 2E10 (June 2017)

31. Takahiro Ogura, Manabu Tanaka, and Hiroyoshi Kawakami, Fabrication and fuel cell properties of nanofiber framework composite membranes bearing continuous proton conductive pathways, The Annual Meeting of the Society of Fiber Science and Technology, Japan, (Tower Hall Funabori), 1P236(June, 2017) (in Japanese)

32. Takahiro Ogura, Takahito Makinouchi, Manabu Tanaka, and Hiroyoshi Kawakami, Fabrication and fuel cell characteristics of nanofiber composite membranes bearing high proton conductive pathways at the interface, The Annual Meeting of the Society of Fiber Science and Technology, Japan, (Tower Hall Funabori), 1F03(June, 2017) (in Japanese)

34. Hiroto Mikami, Yuri Kameyama, Manabu Tanaka, H3royoshi kawakami, Analysis of the CO2 permeation mechanism of polyimide composite containing mixture silica nanoparticles with different morphologies, The Annual Meeting of the Society of Fiber Science and Technology , Tower Hall Funabori, Japan, 2P212 (June, 2017) (in Japanese)

35. Hiroto Mikami, Yuki Kudo, Manabu Tanaka, Hiroyoshi k4wakami, Analysis on the gas permeation mechanism of high gas permeable composite membranes containing surface-modified silica nanoparticles, The Annual Meeting of the Society of Fiber Science and Technology, Tower Hall Funabori, Japan, 2E05 (June, 2017) (in Japanese)

36. Shun Nakazawa, Manabu Tanaka, Hiroyoshi Kawakami, Nanofiber fabrication from lithium single-ion conducting polymers by electrospinning method and their electrolyte application for secondary battery, The Annual Meeting of the Society of Fiber Science and Technology, Japan (Tower Hall Funabori), 2P214 (June 2017)

36. Shun Nakazawa, Tsukasa Watanabe, Manabu Tanaka, Hiroyoshi Kawakami, Fabrication of lithium single-ion-conducting nanofiber framework and their application to secondary batteries, The Annual Meeting of the Society of Fiber Science and Technology, Japan (Tower Hall Funabori), 2E11 (June 2017)

37. Riku KUBOTA, Motoyuki MATSUHO, Shoichiro ASAYAMA, Hiroyoshi KAWAKAMI, Antioxidative activity of novel lactoferrin-modified nanoparticles loaded with potent antioxidant Mn-porphyrins in intranasal brain delivery model *in vitro*(Tsukuba International Congress Cnnter),June 2017.

38. Shoichiro Asayama et al., See the annual report in Japanese (2017).

39. Kohe Arima, Riku Kumota, Shoichiro Asayama, Curative effect of liposome-coated nanoparticle on oxidative stress disease, Biomedical Polymers, Odaiba, Japan (July, 2017)

40. Shoichiro Asayama et al., See the annual report in Japanese (2017).

41. Shoichiro Asayama, Atsushi Nohara, Sakura Taneichi, Yoichi Negishi, Hiroyoshi Kawakami, Design of mono-ion complex for in vivo diffusive plasmid DNA delivery, 44th Annual Meeting & Exposition of the Controlled Release Society, P-436 (Boston, USA) (July, 2017)

42. Riku KUBOTA, Hiroyoshi KAWAKAMI, Novel supramolecular approach for multicatalytic activity of Mn-porphyrin derivative, The 254th ACS National Meeting & Exposition (Washington, D. C., USA), August 2017.

43. Riku KUBOTA, Hiroyoshi KAWAKAMI, Bioinspired water-soluble Mn-porphyrin complex as catalase mimic for antioxidative activity, The 254th ACS National Meeting & Exposition (Washington, D. C., USA), August 2017.

44. Ryosuke Shinohara, Riku Kubota, Shoichiro Asayama, Hiroyoshi Kawakami, Single chain lipid-coated biodegradable polymer nanoparticles having co-delivery activity of drugs / plasmid DNA, the 17th IUPAC International Symposium on MacroMolecular Complexes (MMC-17) (Waseda Univesity), P08(August 28-31, 2017)
45. Yuta Inafune, Manabu Tanaka, Hiroyoshi Kawakami, Fabrication and Characterization of Composite Electrolyte Membranes composed of Lithium Ion Conductive Nanofiber Framework, The 17th IUPAC International Symposium on Macromolecular Complexes (MMC-17), Waseda University, P-41 (August 2017)
46. Kohe Arima, Riku Kumota, Shoichiro Asayama, Effect of liposome-coated nanoparticle possessing antioxidant activity and gene expression capacity on oxidative stress disease, Waseda, Japan, (August, 2017)
47. Takahiro Ogura, Takahito Makinouchi, Manabu Tanaka, and Hiroyoshi Kawakami, Fabrication and Fuel Cell Application of Nafion Composite Membrane Containing Proton Conductive Nanofiber Framework, The 17th IUPAC International Symposium on MacroMolecular Complexes(WASEDA University), (August, 2017)
48. Mikami Hiroto, Shoich hasebe, Manabu Tanaka, Hiroyoshi Kawakami, CO2 Separation Membranes Containing Surface-modified Silica Nanoparticles with Gas Permeable Nano-Space. IUPAC 17th International Symposium on Macro Molecular Complexes (MMC-17), Waseda University, Japan, (August, 2017)
49. Riku KUBOTA, Hiroyoshi KAWAKAMI, Supramolecular system composed of Mn-porphyrin, imidazole and cucurbit[10]uril toward multielectron redox catalyst, The 17th IUPAC International Symposium on MacroMolecular Complexes(Waseda University, Japan), August 2017
50. Shun Nakazawa, Manabu Tanaka, Hiroyoshi Kawakami, Preparation and electrolyte characterizations of nanofiber composite membranes with lithium single-ion conductivity, The 17th IUPAC International Symposium on Macromolecular Complexes (MMC-17), Japan (Waseda University), P-42 (August 2017)
51. Masafumi Yamato, Magnetic field control of low dimensional nano interface array , Meeting of Technical Committee on Biomagnetic and Magnetic Field Effect Studies, Aug. 2017, Tokyo, Japan (in Japanese)
52. Yuta Inafune, Manabu Tanaka, Hiroyoshi Kawakami, Fabrication of lithium ion conductive nanofiber composite electrolyte membranes for all-solid-state lithium ion battery, International Seminar on Green Energy Conversion 2017 , Koumi, P55 (September, 2017)
53. Shun Nakazawa, Manabu Tanaka, Hiroyoshi Kawakami, FABRICATION AND EVALUATION OF LITHIUM SINGLE-ION CONDUCTING NANOFIBER COMPOSITE MEMBRANES, International Seminar on Green Energy Conversion, Japan (Koumi), P-56 (September 2017)
54. Ryosuke Shinohara, Risa Shimazaki, Riku Kubota, Shoichiro Asayama and Hiroyoshi Kawakami, Cell differentiation by epigenetics control aiming diabetes therapy, The 55th Annual Meeting of the Japanese Society for Artificial Organs(Hosei University Ichigaya Campus), YP3-1(September, 2017)
55. Manabu Tanaka, Yuta Inafune, Shun Nakazawa, Kaito Takenaka, Hiroyosi Kawakami, Design and secondary battery application of solid polymer electrolyte based on nanofiber framework, The 66th SPSP Symposium (Ehime University), September 2017.
56. Riku KUBOTA, Hiroyoshi KAWAKAMI, Water-soluble supramolecular system for multielectron redox reaction, The 66th SPSP Symposium(Ehime University),September 2017.
57. Riku KUBOTA, Hiroyoshi KAWAKAMI, Structure-activity relationship for multielectron redox reaction of water-soluble supramolecular system, The 66th SPSP Symposium(Ehime University),September 2017.
58. Shoichiro Asayama et al., See the annual report in Japanese (2017).
59. Shoichiro Asayama, Atsushi Nohara, Sakura Taneichi, Yoichi Negishi, Hiroyoshi Kawakami, Biocompatible highly condensed plasmid DNA for in vivo diffusive delivery, The 25th Anniversary Congress of the European Society of Gene & Cell Therapy, P-380 (Berlin, Germany) (October, 2017)
60. Riku KUBOTA, Hiroyoshi KAWAKAMI, Mechanism of oxygen reduction reaction of water-soluble supramolecular system composed of metalloporphyrin / metallobypiridine / Cucurbit[10]uril, The 67th Conference of Japan Society of Coordination Chemistry(Hokkaido University),September 2017
61. Taiga Takabe, Hideaki Taniguchi, Riku Kubota, Hiroyoshi Kawakami, Structure-activity relationship of novel water-soluble supramolecules composed of metal porphyrin / metal bipyridine / cucurbit [10], The 67th Japan Society of Coordination Chemistry Symposium (Hokkaido university), 1PF-032 (September, 2017) (in Japanese)
62. Manabu Tanaka, Tsukasa Watanabe, Yuta Inafune, Hiroyoshi Kawakamia,Solid Polymer Electrolytes Based on Ion Conductive Nanofiber Framework for Lithium Ion Battery, 232nd ECS MEETING (National Harbor, MD) A01-0064 (October, 2017)
63. Takahiro Ogura, Manabu Tanaka, and Hiroyoshi Kawakami, Fabrication of nanofiber framework composite membranes suitable for low-humidified fuel cell operation, 53th symposium on Polymer and Water Japan(Tokyo Institute of Technology), P8(November, 2017) (in Japanese)
64. Hiroto Mikami, Takuya Muramoto, Yuri Kameyama, Masafumi Yamato, Manabu Tanaka, Hiroyoshi kawakami, Influence of surface-modified nanoparticles on gas permeation properties of polymer composite membranes. 55th symposium of water and polymer, Tokyo Institute of Technology, Japan, P7 (November, 2017) (in Japanese)
65. Kotaro Oyama, Masahumi Yamato,Shoma Mochizuki,Noriyuki Hirota,Hiroyoshi Kawakami, Anisotropic swelling behavior of organic/inorganic hybrid gels prepared in a magnetic field, 55th Symposium on Polymer and Water, Japan,p.23(November, 2017) (in Japanese)
66. Shoichiro Asayama et al., See the annual report in Japanese (2017).
67. Takahiro Ogura, Manabu Tanaka, and Hiroyoshi Kawakami, Fabrication and characterization of acid-doped polybenzimidazole nanofiber composite membranes, 25th Japan Polyimide & Aromatic Polymer Conference(Tokyo Polytechnic University), (November, 2017) (in Japanese)
68. Hiroto Mikami, Manabu Tanaka, Masafumi Yamato, Hiroyoshi kawakami, Gas permeability evaluation of polyimide composite membranes containing mixed silica nanoparticles with different morphologies. 25th symposium of polyimide and Aromatic polymer, Tokyo kougei University, Japan, (November, 2017) (in Japanese)
69. Masafumi Yamato, Shoma Mochizuki, Hiroyoshi Kawakami, and Noriyuki Hirota, Mechanical properties of nanocomposite gel prepared in magnetic field, 87th Musashino area polymer association, Tokyo University of Technology, Poster(November, 2017)(in Japanese)
70. Kazuma Komine, Masafumi Yamato, Hiroyoshi Kawakami,Phase transition enthalpy of nanocomposite gel with different water content,87th Musashino area polymer association, Tokyo University of Technology, Japan, poster (November, 2017) (in Japanese)
71. Masafumi Yamato, Shoma Mochizuki, Hiroyoshi Kawakami, and Noriyuki Hirota, Mechanical properties of nanocomposite gel prepared in magnetic field, 12th Magneto-Science Society of Japan , Kyoto University, Abstract p.112-113 (P-31) (November, 2017) (in Japanese)
72. Masafumi Yamato, Shoma Mochizuki, Hiroyoshi Kawakami, and Noriyuki Hirota, Mechanical properties of nanocomposite gel polymerized in magnetic field,

JSAP-MSSJ-study group of fiscal 2017, Tokyo Metropolitan University Akihabara satellite campus, (P-11) (November, 2017) (in Japanese)
73. Kazuma Komine, Masafumi Yamato, hiroyoshi Kawakami, Thermal analysis of nanocomposite gel, Applied Physics Society The Magneto-Science Society of Japan2017, Tokyo Metropolitan University Akihabara satellitecampus, P-4 (November, 2017) (in Japanese)
74. Takahiro Ogura, Takahito Makinouchi, Manabu Tanaka, and Hiroyoshi Kawakami, Fabrication and Fuel Cell Application of Nanofiber/Nafion Composite Membrane bending proton conductive pathways, The 2nd International Symposium on Hydrogen Energy–based Society (Tokyo Metropolitan University), (November, 2017)
75. Taiga Takabe, Riku Kubota, Hiroyoshi Kawakami, Bioinspired water-soluble Mn-porphyrin complex for catalytic activity, The 2nd International Symposium on Hydrogen Energy–based Society (Tokyo Metropolitan university), P-20 (November, 2017) (in English)
76. Mikami Hiroto, Shoich hasebe, Manabu Tanaka, Hiroyoshi Kawakami, CO2 Separation Membranes Containing Surface-modified Silica Nanoparticles for High Gas Permeation. The 2nd International Symposium on Hydrogen Energy–based Society. Tokyo Metropolitan University, Japan, (November, 2017)
77. Manabu Tanaka, Yuta Inafune, Shun Nakazawa, Kaito Takenaka, Hiroyoshi Kawakami, Fabrication and Secondary Battery Application of Solid Polymer Electrolytes Based on Lithium Ion Conductive Nanofiber Framework, The 58th Battery Symposium (Kyushu International Conference Center) 3C05 (December, 2017)
78. Shoichiro Asayama et al., See the annual report in Japanese (2017).
79. D. Katayama, R. Fujihara, T. Ando, N. Hirota, O. Koike, R. Tatsumi, M. Yamato, Numerical simulation of structure formation of magnetic particles in solvent under magnetic fields toward development of anisotropic materials, 11th Annual Meeting of the Magneto-Science Society of Japan, Nov. 2017, Kyoto, Japan (in Japanease)

■Patents

1. P2017-63039, Polymer Electrolyte Membrane and Fuel Cell, Hiroyoshi Kawakami, Manabu Tanaka, Tsukasa Watanabe
2. Hiroyoshi Kawakami, Shoichiro Asayama, Shohei Yamaguchi, Motoyuki Matsuho, Yutaro Asaba, See the annual report in Japanese.
3. P2017-216187, Blend Nanofiber and Their Composite Membrane, Hiroyoshi Kawakami, Manabu Tanaka, Risa Sakaguchi
4. WO/2017/179738, Fabrication Method of Gas Separation Membrane, Hiroyoshi Kawakami, Manabu Tanaka, Yuri Kameyama, Azusa Osawa, Tadayuki Isaji, Takamasa Kikuchi
5. Shoichiro Asayama, Hiroyoshi Kawakami, Kana Nagashima, Yuya Sone, See the annual report in Japanese

■Awards

1. Student Poster Award, 39th Annual Meeting on The Membrane Society of Japan, Yuta Inafune, Manabu Tanaka, Hiroyoshi Kawakami, Fabrication and evaluation of bipolar stacked all-solid-state secondary battery with lithium ion conductive nanofiber composite electrolyte membranes
2. Student Poster Award, 39th Annual Meeting on The Membrane Society of Japan, Shun Nakazawa, Manabu Tanaka, Hiroyoshi Kawakami, Preparation and secondary battery characterizations of lithium single-ion conducting nanofiber composite membrane
3. Student Poster Award, The Annual Meeting of the Society of Fiber Science and Technology, Japan, Yuta Inafune, Manabu Tanaka, Hiroyoshi Kawakami, Fabrication and evaluation of multi stacked all-solid-state secondary battery comprising of lithium conductive nanofiber composite electrolyte membranes
4. Most Excellent Poster Award, The 55th Annual Meeting of the Japanese Society for Artificial Organs, Ryosuke Shinohara, Risa Shimazaki, Riku Kubota, Shoichiro Asayama and Hiroyoshi Kawakami, Cell differentiation by epigenetics control aiming diabetes therapy
5.Hiroyoshi Kawakami, ACS Publication Awards, ACS.
6.Hiroyoshi Kawakami, 2018 Albert Nelson Marquis Lifetime Achievement Award, MARQUIS WHOS WHO.

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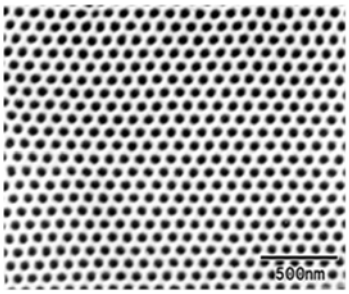
Bachelor 4 -8

■Outlines of the Research

(1) Fabrication of Nanofilters by Electrochemical Process
Hideki MASUDA, Takashi YANAGISHITA

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



SEM image of anodic porous alumina

(2) Preparation of Ordered Nanostructures by Nanoimprinting Using Ordered Anodic Porous Alumina Molds
Hideki MASUDA, Takashi YANAGISHITA

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

(3). Fabrication of Enagy Devices Based on Ordered Anodic Porous Alumina
Hideki MASUDA, Takashi YANAGISHITA

For the preparation of uniform sized nanoparticles, we have introduced membrane emeulsification process using ordered anodic porous alumina. The present process is simple and can be used as a high-throughput process for forming monodispersed nanoparticles of metal oxides. The monodispersed nanoparticles prepared by this process will be useful as electrode active materials in the Li ion batteries to improve the properties.

(4) Study of Self-ordering Mechanism of the Cell Arrangement of Anodic Porous Alumina
Hideki MASUDA, Toshiaki KONDO

Regularity of the holearray structure of the anodic porous alumina which is used as mother template is important to improve the regularity of the obtained metal and semiconductor nanohole arrays. To improve the regularity of the holearray structure of the anodic porous alumina, anodizing conditions were explored, and self-ordering of the anodic oxide film was newly discovered in sulfuric acid solution. The detailed mechanism of the self-ordering of the anodic porous alumina is currently being investigated.

(5)Evaluation of Pore Structures of Highly Ordered Porous Alumina by Nitrogen Adsorption Method
Takashi Takei, Takashi Yanagishita, Hideki Masuda

The pore size distribution and surface area of highly ordered porous alumina have been investigated by the nitrogen adsorption method.

■Papers with Peer Review

1. Takashi Yanagishita, Masahiko Imaizumi, Toshiaki Kondo, and Hideki Masuda
   Preparation of Nanoporous Alumina Hollow Spheres with a Highly Ordered Hole Arrangement
   RSC Adv., 8, 2041 (2018).

2. Takashi Yanagishita, Toshiaki Kondo, and Hideki Masuda
   Preparation of Renewable Antireflection Moth-Eye Surfaces by Nanoimprinting Using Anodic Porous Alumina Molds
   J. Vac. Sci. Technol. B, in press.

3. Takashi Yanagishita, Taito Inoue, Toshiaki Kondo, and Hideki Masuda
   Preparation of Monodisperse $LiCoO_2$ Hollow Particles by Membrane Emulsification Using Anodic Porous Alumina
   Chem. Lett., in press.

4. Takashi Yanagishita, Masahiko Imaizumi, Toshiaki Kondo, and Hideki Masuda
   Formation of Porous Al Particles by Anisotoropic Etching
   Electrochem. Commun., 78, 26 (2017).

5. Toshiaki Kondo, Hayato Miyazaki, Takashi Yanagishita, and Hideki Masuda
   Anodic Porous Alumina with Square Holes Through Lattice Conversion of Naturally Occurring Ordered Structure
   J. Vac. Sci. Technol. B, 35, 050602 (2017).

6. Toshiaki Kondo, Sanami Nagao, Takashi Yanagishita, and Hideki Masuda
   Tuning of Interval in Nanohole Array of Anodic Porous Alumina through Deformation of Polymer Templates
   RSC Adv., 7, 44799 (2017).

7. Nhat Truong Nguyen, Imgon Hwang, Toshiaki Kondo, Takashi Yanagishita, Hideki Masuda, and Patrik Schmuki
   Optimizing TiO_2 Nanotube Morphology for Enhanced Photocatalytic H_2 Evolution Using Single-Walled and Highly Ordered TiO_2 Nanotubes Decorated with Dewetted Au Nanoparticles
   Electrochem. Commun, 79, 46 (2017).

8. Takashi Yanagishita, Atsushi Kato, and Hideki Masuda
   Preparation of Ideally Ordered Through-Hole Anodic Porous Alumina Membranes by Two-Layer Anodization
   Jpn. J. Appl. Phys., 56, 035202 (2017).

9. Ryohei Takakura, Tomoya Oshikiri, Kosei Ueno, Xu Shi, Toshiaki Kondo, Hideki Mausda, and Hiroaki Misawa
   Water Splitting Using a Three-Dimensional Plasmonic Photoanode with Titanium Dioxide Nano-Tunnels
   Green Chem, 19, 2398 (2017).

10. A. Kawamura, S. Ueno, C. Takai, T. Takei, H.Razavi-Khosroshahi, M. Fuji
    Effect of steric hindrance on surface wettability of fine silica powder modified by n- or t-butyl alcohol
    Adv.Powder.Technol., 28, 2488 (2017)

■Reviews and Books
See the annual report in Japanese (7 articles)

■Invited Lectures
＊International

1. Hideki Masuda, Toshiaki Kondo ,and Takashi Yanagishita
   Synthesisi of Ordered Semiconductor Nanostructures for Energy Conversion Using Anodic Porous Alumina
   231th ECS Meeting, 2017/5, New Orleans, US.

2. Hideki Masuda, Toshiaki Kondo ,and Takashi Yanagishita
   Highly Ordered Anodic Porous Alumina for Functioanl Nanodevices
   Anodizing it 2017 congress, 2017/7, Toulouse, France

3. Hideki Masuda
   Preparation of Ordered Micro- and Nanostructures for Functional Devices by Using Anodic Porous Alumina
   2nd Global Congress & Expo on Materials Science & Nanoscience, , 2017/9, Valencia, Spain

4. Takashi Yanagishita
   Anodizing Process for Hydrogen Energy Synthesis
   The 2nd International Symposium on Hydrogen Energy-based Society, 2017/11, Tokyo

5. Toshiaki Kondo, Takashi Yanagishita, Hideki Masuda
   Ideally Ordered Nanohole Array Obtained by Anodizing Pretextured Metals
   Electrochemistry 2017, 2017/11, Berlin

6. Toshiaki Kondo, Takashi Yanagishita, Hideki Masuda
   Fabrication of Al Nanowires Based on Anodic Porous Alumina and Its Plasmonic Properties
   The 39th PIERS, 2017/11, Singapore

＊Domestic
See the annual report in Japanese (8 articles)

■Academic Meeting
＊International

1. Takashi Yanagishita, Atsushi Kato, Toshiaki Kondo, Hideki Masuda,
   Fabrication of Ordered Porous Alumina Through-Hole Membrane by Two-Layer Anodization
   2017 MRS Fall Meeting, 2016/11, Boston

2. Toshiaki Kondo, Taiga Sakamoto, Takashi Yanagishita, and Hideki Masuda,
   Fabrication of Ordered Array of ZnO Nanorods Using Anodic Porous Alumina
   2017 MRS Fall Meeting, 2016/11, Boston

＊Domestic
See the annual report in Japanese (23 articles)

■Patents
See the annual report in Japanese (12 articles)

■Awards
See the annual report in Japanese (1 articles)

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Master's course -6
Bachelor 4 -4

■Outlines of the Research

Development of Highly Designed Organic Molecules

Wataru SETAKA, and Yusuke INAGAKI

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

1. Crystalline Molecular Gyrotop

A molecular machine has been defined as a discrete number of molecular components that perform mechanical–like movements in response to specific stimuli. A macrocage molecule with a bridged thiophene rotor was synthesized as a molecular gyrotop having a dipolar rotor, given that the dipole derived from the thiophene can rotate even in the crystal. The thermally induced change in the orientation of the dipolar rotors (thiophene ring) inside the crystal, *i.e.*, order-disorder transition, and the variation in the optical properties in the crystalline state were observed.

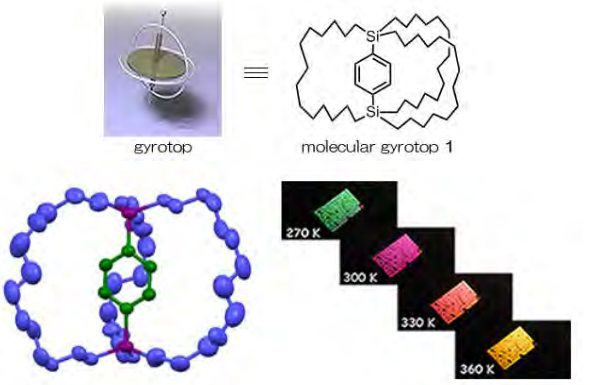

Figure. Structure of molecular gyrotop and birefringence change.

2. Novel Molecular Bevel Gears

Bis(9-triptycyl)X systems (X= CH2, O, NH, SiH2, PH, etc.) are known as well-designed bevel gear systems. To use the gear systems as a molecular machine, it is desirable to introduce a clutch-declutch mechanism controllable by external stimuli. Silane-silicate interconversion using reversible attachment of a fluoride ion may be a promising option for this purpose. We investigate that the introduction of the clutch-declutch mechanism into a new gear system, a bis(9-triptycyl)difluorosilane derivative, is achieved by the reversible attachment of a fluoride ion.

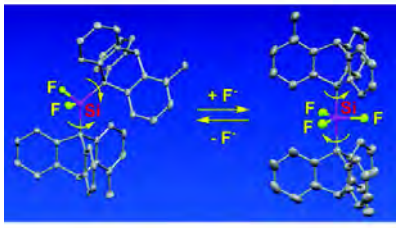

Figure. Cluch-decluch function in a novel molecular gear.

3. Control of Intramolecular Charge-Transfer Fluorescence

Phenyldisilanes show unique intramolecular charge- transfer fluorescence. To control of its fluorescence intensity with addition of alkali metal cation, we synthesized aminomethyl-substituted phenyldisilane 1. The fluorescence of 1 was quenched by photoinduced electron transfer (PET) from internal nitrogen atom. However, the intense fluorescence of 1 was observed in the presence of Na^+, because coordination of Na^+ to amino group prevents the quenching. These results indicates that the controlling of the ICT fluorescence intensity is achieved by utilizing PET mechanism.

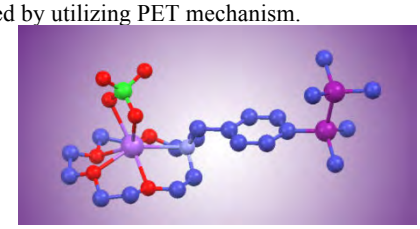

Figure. A phenyldisilane which exhibits CT fluorescence.

■Papers with Peer Review

1. A Crystalline Molecular Gyrotop with a Biphenylene Dirotor and its Temperature Dependent Birefringence, A. Fujiwara, Y. Inagaki, H. Momma, E. Kwon, K. Yamaguchi, M. Kanno, H. Kono, and W. Setaka, *Cryst. Eng. Comm.,* 19, 6049-6056 (2017).

■Account

1. Phenylene-bridged Macrocages as Molecular Gyrotops, Wataru Setaka, *Organosilicon Chemistry*, 34, 19-26 (2017).

■Invited Lectures

1. Wataru Setaka, Phenylene-bridged Macrocages as Crystalline Molecular Gyrotops, International Conference of Natural and Artificial Molecular Machines, 2017.12.18-20, IIT Bombay, India (IT11 12/19, invited)

■Awards

1. Taro Tsuchiya received the excellent poster award at 7th CSJ Chemistry Festa, the Chemical Society of Japan (17-19 October 2017, Funabori (Tokyo)). The title of her presentation was "Synthesis of a o-Difluorobenzene-bridged Molecular Gyrotop".

■Academic Meeting

1. Noriyuki Tanaka, Yusuke Inagaki, Kentaro Yamaguchi, Wataru Setaka
Synthesis and Crystal Structure of a Resorcyltriptycene
The 98th CSJ Annual Meeting, Funabashi Campus, Nihon University (Funabashi, Chiba) (oral)

2. Satoshi Hosono, Yusuke Inagaki, Wataru Setaka
Synthesis of Tin-linked Molecular Bevel Gears and Observation of Gear Slippage
The 98th CSJ Annual Meeting, Funabashi Campus, Nihon University (Funabashi, Chiba) (oral)

3. Masaya Ito, Yusuke Inagaki, Kentaro Yamaguchi, Wataru Setaka
Synthesis of a Bipyridylene-bridged Molecular Gyrotop and Formation of its Palladium Complex
The 98th CSJ Annual Meeting, Funabashi Campus, Nihon University (Funabashi, Chiba) (oral)

4. Daiki Hayashi, Yusuke Inagaki, Wataru Setaka
Synthesis and Photophysical Properties of Silyl-substituted Thieno[3,2-b]thiophenes
The 98th CSJ Annual Meeting, Funabashi Campus, Nihon University (Funabashi, Chiba) (oral)

5. Hikaru Hashimoto, Yusuke Inagaki, Wataru Setaka
Preparation and ESR observation of N-oxyl Carbazole bridged Macrocages
The 98th CSJ Annual Meeting, Funabashi Campus, Nihon University (Funabashi, Chiba) (oral)

6. Kajiyama Kazuki, Inagaki Yusuke, Yamaguchi Kentarou, Setaka Wataru
Synthesis of Phenylene-bridged Diazamacrocycles and their Redox Property
The 98th CSJ Annual Meeting, Funabashi Campus, Nihon University (Funabashi, Chiba) (oral)

7. Taro TSUCHIYA, Yusuke INAGAKI, Kentaro YAMAGUCHI, Wataru SETAKA
Synthesis of a o-Difluorobenzene-bridged Molecular Gyrotop and its Rotational Dynamics in a Crystalline State
The 98th CSJ Annual Meeting, Funabashi Campus, Nihon University (Funabashi, Chiba) (oral)

8. Hikaru Hashimoto, Yusuke Inagaki, Kentaro Yamaguchi, Wataru Setaka
Novel Functions of a Carbazole in Carbazole Bridged Macrocages
The 44th Symposium on Main Group Element Chemistry, Tokyo Inst. of Tech., 12.7-9, 2017 (oral)

9. Hideaki Takashima, Yusuke Inagaki, Kentaro Yamaguchi, Wataru Setaka
Synthesis and Redox Properties of Ferrocene or Ruthenocene Bridged Macrocages
The 44th Symposium on Main Group Element Chemistry, Tokyo Inst. of Tech., 12.7-9, 2017 (poster)

10. Taro Tsuchiya, Yusuke Inagaki, Kentaro Yamaguchi, Wataru Setaka
A Novel 1,2-Difluorophenylene Bridged Molecular Gyrotop as a Candidate for Dielectric Material
The 2nd International Symposium on Hydrogen Energy-based Society, 2017.11.20-21, Tokyo Metropolitan University, Japan (poster)

11. Taro TSUCHIYA, Yusuke INAGAKI, Wataru SETAKA
a o-Difluorobenzene-bridged Molecular Gyrotop
7th Chemistry CSJ Fesrta, Tower Hall Fumabori, 10.17-19, 2017. (poster)
*Best Poster Award

12. Noriyuki Tanaka, Yusuke Inagaki, Kentaro Yamaguchi, Wataru Setaka
Synthesis of a Resorcyltriptycene as a Novel Molecular Rotor
7th Chemistry CSJ Fesrta, Tower Hall Fumabori, 10.17-19, 2017. (poster)

13. Masaya Ito, Yusuke Inagaki, Wataru Setaka
Synthesis of a Bipyridylene-bridged Molecular Gyrotop and its Palladium Complex
7th Chemistry CSJ Fesrta, Tower Hall Fumabori, 10.17-19, 2017. (poster)

14. Miyako Tsurunaga, Junko ARASE, Yusuke INAGAKI, Kentaro YAMAGUCHI, Wataru SETAKA
Dielectric Properties of Thiophene Dioxide Bridged Molecular Gyrotop in a Crystalline State
28th Symposium on Physical Organic Chemistry, Kyusyu University, 9.7, 2017. (oral)

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Master's course -2

■Outlines of the Research

1. Gas Phase Reactions by Metal Oxide-Supported Gold Catalysts

Toru MURAYAMA, Takuya YOSHIDA, Yasunori INOUE, Sinichi HATA, Mingyue LIN, Qianqian ZHU, Tamao ISHIDA, Masatake HARUTA

Gold clusters were deposited on a Keggin-type polyoxometalate by sol immobilization. Deposition of Au clusters smaller than 2 nm onto $Cs_4SiW_{12}O_{40}$ was essential to show high catalyitc activity for CO oxidation. The Au/$Cs_4SiW_{12}O_{40}$ showed extreamly high stability for at least one month at 0 °C with full conversion. The catalytic activity drastically changed at temperatures higher than 40 °C, showing a unique behavior called a U-shaped curve (Fig. 1). The reaction mechanism changed in accordance with the temperature range. It was revealed that the adsorption of water around gold promoted CO oxidation at temperatures of less than 60 °C.

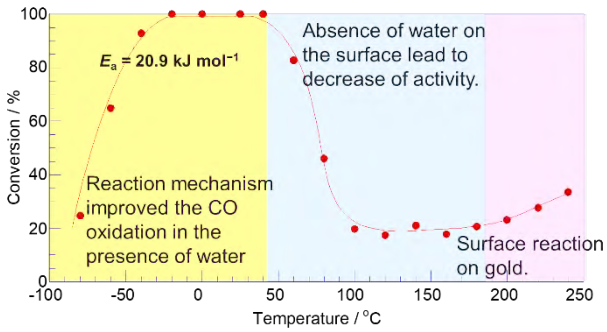


Figure 1. Effects of reaction temperature on CO oxidation over Au/$Cs_4SiW_{12}O_{40}$.

For efficient elimination of odors, selective oxidations were carried out using various kinds of supported gold catalysts. The selectivity depended on the kinds of support.

Catalysts that realize the NH_3-selective catalytic reduction (NH_3-SCR) under mild conditions are demanded in the NO removal technologies. The V_2O_5 catalyst that we developed

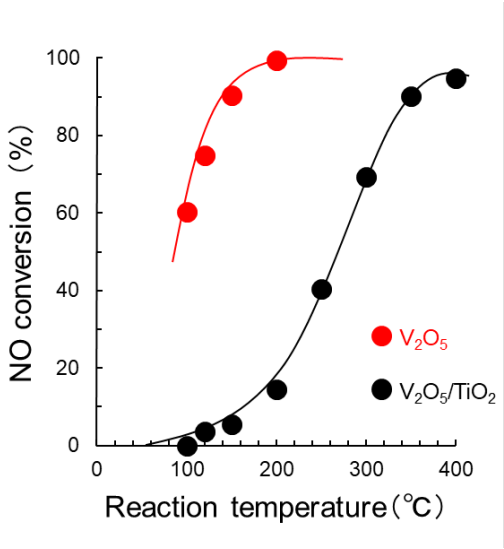


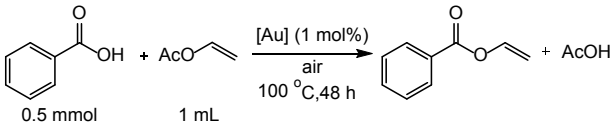
Figure 2. Dependence of NO conversion on reaction temperature in SCR of NO with NH_3 using V_2O_5 and 2-3 wt%V_2O_5/TiO_2.

showed extremely high denitrification rate at 200 ˚C or less by the increase of acid sites due to the high specific surface area, indicating that pure V_2O_5 with high specific surface area has higher activity than conventional industrial catalysts (2-3wt% V_2O_5/TiO_2) in the low temperature range. These results are expected to greatly contribute to the efficiencent improvement of the exhaust gas treatment system and is highly appreciated in a wide range of fields such as catalytic chemistry and process engineering.

2. Liquid Phase Reactions by Supported Metal Nanoparticle Catalysts

Tamao ISHIDA, Ayako TAKETOSHI, Masatake HARUTA

We have found that oxidative sp^2 C–H bond coupling for synthesis of biaryls was catalyzed by supported gold nanoparticles via electrophilic aromatic substitution reaction, which takes place on the cationic gold atoms at the perimeter interface with metal oxide supports. It has been also revealed by theoretical chemistry that zero valent gold nanoparticles have soft Lewis acidity. In this work, to evaluate the soft Lewis acidity of gold nanoparticles, we examined transfer vinylation of carboxylic acids with vinyl acetate which is traditionally catalyzed by homogeneous Au(I) catalysts (Scheme 1).



Scheme 1. Transfer vinylation of benzoic acid with vinyl acetate.

We screened various kinds of metal oxide supported gold catalysts (Au 1 wt%). Figure 3 shows the relationships between acid-base properties of metal oxide supports and the product yield. As a result, gold particles on acidic and basic supports showed inferior catalytic activity to those on amphoteric ones, and Au/ZrO_2 gave the highest yield. A decrease in Au loading to 0.3 wt% improved the yield due to a decrease in gold particle size. The use of mixed-metal oxide, CeO_2-ZrO_2, further improved the catalytic activity of gold to give vinyl benzoate up to 92%.

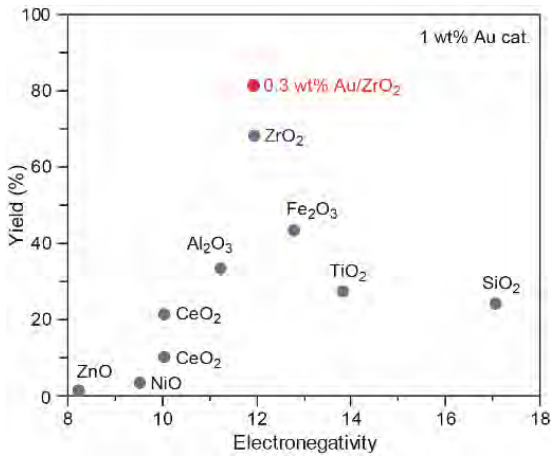


Figure 3. Relationships between electronegativity of metal oxide supports and the yield of vinyl benzoate.

The active Au species was also evaluated using Au/CeO_2-ZrO_2 having different Au(III)/Au(0) ratio. Au(0) on CeO_2-ZrO_2 showed superior activity to Au(III) as a major species. In addition, smaller Au(0) nanoparticles exhibited better performance than larger ones. From these results, Au(0) nanoparticles can work as soft Lewis acid catalysts and the activity was better than cationic Au when they are supported on metal oxides.

Aliphatic esters are important compounds as flavors and fragrance. In industry, esters are produced by two steps, oxidation of aldehyde to carboxylic acid followed by acid-catalyzed esterification. From the point of view of green chemistry, oxidative esterification by one step has been attracting attention. We chose oxidative esterification of octanal with ethanol as a model reaction to give ethyl octanoate. Various kinds of supported gold catalysts have been screened in a batch reactor (Fig. 4). After reaction for 5 h, ethyl octanoate was obtained in high yields with high selectivities by Au/ZnO, Au/Al_2O_3, and Au/SiO_2. Next, the reaction was carried out in a continuous flow reactor. The catalytic activity could be maintained for at least 6 h.

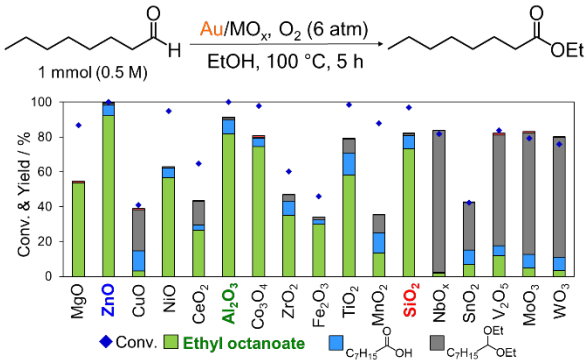


Figure 4. Oxidative esterification of octanal with ethanol catalyzed by gold nanoparticles.

3. Synergistic Effects of Gold Nanoparticle Catalysts with Biofunctional Materials

Jun-ichi NISHIGAKI, Takashi FUJITA, Masatake HARUTA

3-1. Enzyme/Gold Hybrid Catalysts

We developed the catalytic reactions showing synergistic/complementary effects by combining biological and artificial Au nanoparticle catalysts together. Nicotinamide adenine dinucleotide (NADH as a reduced form and NAD^+ as an oxidized one) works as a coenzyme that is comsumed in enzymatic reactions. Generally, stoichiometric amout of $NADH/NAD^+$ is required, so that a lot of amount of waste was produced after the reactions. If the catalytic recycling of $NADH/NAD^+$ is realized, the use of coenzymes can be significantly decreased, contributing green chemistry. We studied the catalytic reduction of NAD^+ to NADH by supported Au catalysts using H_2. Small Au clusters (<2 nm) deposited on basic supports (Au/CeO_2 and Au/hydrotalcite (HT)) hydrogenated NAD^+ under 1.0 MPa H_2 to form NADH (Fig. 5). The hydrogenation activity of Au catalysts was lower than that of PtAu alloy catalysts, but NADH selectivity was higher. It suggests that H_2 was heterolytically activated on the interface of Au clusters and basic supports. Now we synthesize smaller Au cluster catalysts to improve the catalytic performance and screen the support materials which do not inhibit dehydrogenase activity in the aim of enzyme/coenzyme/Au hybrid catalytic systems to achieve in-situ coenzyme regeneration.

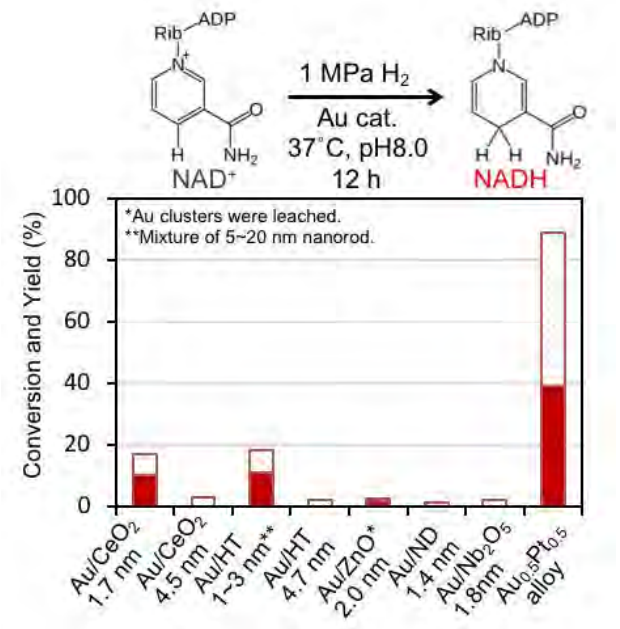


Figure 5. Hydrogenation of NAD^+ by gold catalysts.

3-2. Biomedical Application of Gold Catalysts

For biomedical application of Au nanoparticle catalysts, we examined the cytotoxic and inflammatory response of macrophagic cells exposed to Au/MO_x. Mice peritoneal primary macrophages were exposed to 1–100 μg/mL particles of Au/TiO_2 and TiO_2 for 48 h. Neither Au/TiO_2 nor TiO_2 showed showed cytotoxicity to the macrophagic cells by MTT and lactic acid dehydrogenase (LDH) assays. With regard to the inflammatory response, a significant increase in TNF-α secretion was observed by exposure to TiO_2 but was much less pronounced for Au/TiO_2. To examine this effect of Au/TiO_2 in detail, lipopolysaccharide (LPS)-induced pro-inflammatory response was measured (Fig. 6).

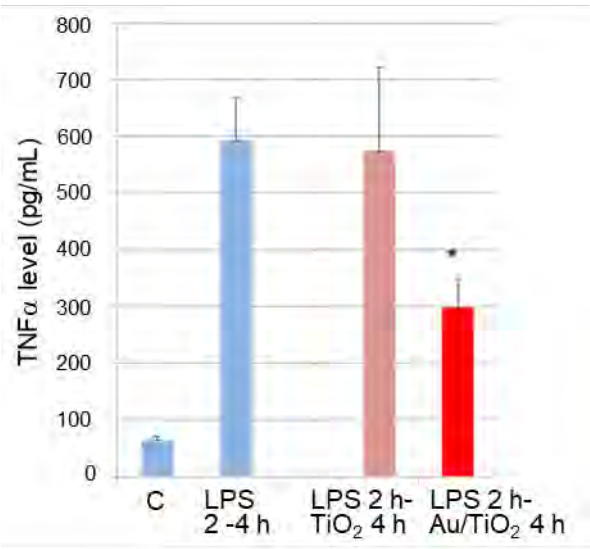


Figure 6. TNFα levels after LPS-induced inflammation and exposition of machrophagic ceslls to Au/TiO_2 and TiO_2. C: control experiment.

When TiO_2 was added to the macrophagic cells, the amount of the pre-existing TNF-α was almost consistent with that of the LPS-induced control experiment. In contrast, the amount of TNF-α was significantly decreased by adding Au/TiO_2. This result suggests that Au/TiO_2 attenuates LPS-induced inflammation. The similar effet was also observed on Au/ZrO_2. Although the Au-mediated anti-inflammatory mechanism remains unclear at this stage, this study revealed that Au/TiO_2 and Au/ZrO_2 are promising candidates for anti-inflammatory agents.

4. Catalytic Reaction System in Interfacial DNA Film Integrated with Gold Nanoparticles and Enzymes

Daisuke ISHIKAWA, Masatake HARUTA

A lattice-shaped DNA nanostructure capable of selectively introducing gold catalysts and enzymes was prepared by using DNA origami method (Fig. 7a). In this nanostructure, it is possible to fix catalysts modified with single-stranded DNA by using the hybridization at a designed location. The optimal salt concentration and annealing conditions for producing this structure have been determined from many electrophoresis analyses (Fig. 7b).

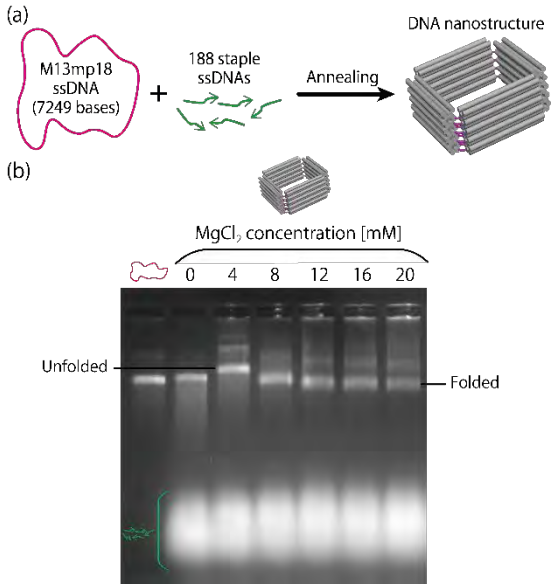


Figure 7. (a) Schematic illustration of the lattice-shaped DNA nanostructure, (b) Determination of $MgCl_2$ concentration for prepation of the DNA nanostructure.

■Papers with Peer Review

1. A. Taketoshi, T. Ishida, H. Ohashi, T. Honma, M. Haruta, "Preparation of gold clusters on metal oxides by deposition-precipitation with microwave drying and their catalytic performance for CO and sulfide oxidation", *Chin. J. Catal.* **2017,** *38*, 1888–1898.
2. Q. Lin, C. Han, H. Su, L. Sun, T. Ishida, T. Honma, X. Sun, Y. Zheng, C. Qi, "Remarkable enhancement of Fe-V-O_x composite metal oxide to gold catalyst for CO oxidation in the simulated amosphere of CO_2 laser", *RSC Adv.* **2017**, *7*, 38780–38783.
3. Z. Zhang, Y. Kumamoto, T. Hashiguchi, T. Mamba, H. Murayama, E. Yamamoto, T. Ishida, T. Honma, M. Tokunaga, "Wacker Oxidation of Terminal Alkenes over ZrO_2 Supported Pd Nanoparticles under Acid- and Co-Catalyst-Free Conditions", *ChemSusChem* **2017**, *10*, 3482–3489.
4. H. Murayama, T. Hasegwa, Y. Yamamoto, M. Tone, M. Kimura, T. Ishida, T. Honma, M. Okumura, A. Isogai, T.

Fujii, M. Tokunaga, "Chloride-Free and Water-Soluble Au Complexes for Preparation of Supported Small Nanoparticles by Impregnation Method", *J. Catal.* **2017**, *353*, 74–80.
5. H. Ando, D. Kawamoto, H. Ohashi, T. Honma, T. Ishida, Y. Okaue, M. Tokunaga, T. Yokoyama, "Adsorption Behavior of Au(III) Complex Ion on Nickel Carbonate and Nickel Hydroxide", *Colloids Surf. A* **2018**, *537*, 383–389.
6. T. Ishida, Z. Zhang, H. Murayama, M. Tokunaga, "Oxide-Supported Palladium and Gold Nanoparticles for Catalytic C-H Transformations", *J. Synth. Org. Chem., Jpn.* **2017**, *75*, 1150–1161.
7. A. Yada, T. Murayama, J. Hirata, T. Nakashima, M. Tamura, Y. Kon, W. Ueda, "W-Ti-O Mixed Metal Oxide Catalyzed Dehydrative Cross-etherification of Alcohols", *Chem. Lett.* **2018**, *in press*.
8. T. Yoshida, T. Murayama, N. Sakaguchi, M. Okumura, T. Ishida, M. Haruta, "Carbon Monoxide Oxidation by Polyoxometalate-Supported Gold Nanoparticulate Catalysts: Activity, Stability, and Temperature-Dependent Activation Properties", *Angew. Chem. Int. Ed.* **2018**, *57*,1523–1527.
9. K. Nakajima, J. Hirata, M. Kim, N. K. Gupta, T. Murayama, A. Yoshida, N. Hiyoshi, A. Fukuoka, W. Ueda, "Facile Formation of Lactic Acid from a Triose Sugar in Water over Niobium Oxide with a Deformed Orthorhombic Phase", *ACS Catal.* **2018**, *8*, 283–290.
10. T. Baidya, T. Murayama, P. Bera, O. Safonova, P. Steiger, N. Katiyar, K. Biswas, M. Haruta, "Low-temperature CO oxidation over combustion made Fe and Cr doped Co_3O_4 catalysts: Role of dopant's nature toward achieving superior catalytic activity and stability", *J. Phys. Chem. C* **2017**, *121*, 15256–15265.
11. S. Ishikawa, Y. Goto, Y. Kawahara, S. Inukai, N. Hiyoshi, N. F. Dummer, T. Murayama, A. Yoshida, M. Sadakane, W. Ueda, "Synthesis of crystalline microporous Mo-V-Bi oxide for selective (amm)oxidation of light alkanes", *Chem. Mater.* **2017**, *29*, 2939–2950.
12. T. Murayama, K. Nakajima, J. Hirata, K. Omata, E. J. M. Hensen, W. Ueda, "Hydrothermal Synthesis of a Layered-type W-Ti-O Mixed Metal Oxide and its Solid Acid Activity", *Catal. Sci. Tech.* **2017**, *7*, 243–250.
13. S. Ishikawa, D. Jones, S. Iqbal, R. Christian, D. J Morgan, D. J. Willock, P. Miedziak, J. K. Bartley, J. Edwards, T. Murayama, W. Ueda, G. Hutchings, "Identification of the catalytically active component of Cu-Zr-O catalyst for the hydrogenation of levulinic acid to γ-valerolactone"', *Green Chem.* **2017**, *19*, 225–236.
14. K. Nomiya, K. Endo, Y. Murata, S. Sato, S. Shimazaki, S. Horie, E. Nagashima, Y. Yasuda, T. Yoshida, S. Matsunaga, T. Matsubara, "Polyoxometalate-Assisted, One-Pot Synthesis of a Pentakis[(triphenylphosphane)gold]ammonium(2+) Cation Containing Regular Trigonal-Bipyramidal Geometries of Five Bonds to Nitrogen", *Inorg. Chem.* **2018**, *57*, 1504–1516.
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16. T. Sagami, S. Umemoto, Y. O. Tahara, M. Miyata, Y. Yonamine, D. Ishikawa, T. Mori, K. Ariga, H. Miyake, S. Shinoda, "pH-Responsive Cotton Effects in the d-d Transition Band of Self-Assembling Copper (II) Complexes with a Cholesteryl-Armed Ligand", *Bull. Chem. Soc. Jpn.*, **2017**, *90*, 739–745.
17. T. Mori, D. Ishikawa, Y. Yonamine, Y. Fujii, J. P Hill, I. Ichinose, K. Ariga, W. Nakanishi, "Mechanically Induced Opening-Closing Movements of Binaphthyl Molecular Pliers: Digital Phase Transition v.s. Continuous Conformational Change", *ChemPhysChem*, **2017**, *18*, 1470–1477.
18. S. Hata, T. Omura, K. Oshima, Y. Du, Y. Shiraishi, N. Toshima, "Novel Preparation of Poly(3,4-ethylene dioxythiophene)-Poly(styrenesulfonate)-Protected Noble Metal Nanoparticles as Organic-Inorganic Materials", *Bull. Soc. Photogr. Imag. Jpn.* **2017**, *27*, 13-18.
19. M. Sadakiyo, S. Hata, X. Cui, M. Yamauchi, "Electrochemical Production of Glycolic Acid from Oxalic Acid Using a Polymer Electrolyte Alcohol Electrosynthesis Cell Containing a Porous TiO_2 Catalyst", *Sci. Rep.* **2017**, *3*, 17032.
20. Y. Shiraishi, S. Hata, Y. Okawauchi, K. Oshima, H. Anno, N. Toshima, "Improved Thermoelectric Behavior of Poly(3,4-ethylene dioxythiophene)-Poly(styrenesulfonate) using Poly(*N*-vinyl-2-pyrrolidone)-coated GeO_2 Nanoparticles", *Chem. Lett.* **2017**, *46*, 933–936.
21. T. Fukushima, S. Kitano, S. Hata, M. Yamauchi, "Carbon neutral energy cycles using alcohols", *Sci. Tech. Adv. Mater.* **2018**, *19*, 142–152.

■Books

1. T. Ishida, M. Haruta, "Supported Gold Nanoparticles Leading to Green Chemistry", in Nanotechnology in Catalysis: Applications in the Chemical Industry, Energy Research, and Environment Protection, B. F. Sels, M. van de Voorde, Eds., Wiley-VCH, 2017, pp. 21–36.

■Invited Lectures

1. T. Fujita, M. Haruta, J. Boczkowski, "Gold catalysis: a new anti-inflammaging therapeutic option", JSPS-INSERM Joint Symposium, Paris, France, 2017.7.3.
2. T. Ishida, "Palladium and Gold-Nanoparticle-Catalyzed Oxidative C-H Functionalization", 8th World Congress on Oxidation Catalysis (2017) (8WCOC), Krakow, Poland, 2017.9.5.
3. T. Murayama, H. Gi, K. Shinzato, M. Sadakane, H. Miyaoka, T. Ichikawa, "Hydrogen desorption and absorption in MgH_2 assisted by catalytic effect of Nb_2O_5", The 2nd International Symposium on Hydrogen Energy–based Society, Tokyo Metropolitan University, 2017.11.21.
4. A. Taketoshi, "Oxidative Esterification of Octanal Catalyzed by Gold Nanoparticles in Batch and Continuous Flow Reactors", TMU and PetroMat Joint Mini Symposium on Catalysis and Advanced Materials 2018, Tokyo Metropolitan University, 2018.1.31.

The other four invite lectures in Japan are written in Japanese version.

■**Academic Meeting**

＊**International (oral)**

1. T. Murayama, K. Nakajima, N. K. Gupta, A. Fukuoka, M. Haruta, “Gold nanoparticulate catalysts deposited on niobium oxide and their catalytic activity for gas and liquid phase oxidation”, 8th International Symposium on Acid-Base Catalysis (ABC-8), Rio de Janeiro, Brazil, 2017.5.9.
2. H. Gi, K. Shinzato, M. Sadakane, T. Murayama, H. Miyaoka, T. Ichikawa, “Catalytic effect of various Nb_2O_5 on hydrogen desorption and absorption in MgH_2”, The 1st International Symposium on Fuels and Energy, Hiroshima, Hiroshima, 2017.7.11.
3. T. Murayama, K. Nakajima, N. K. Gupta, A. Fukuoka, M. Haruta, “Low temperature gas/liquid phase oxidation by nanoparticulate gold catalysts deposited on niobium oxide”, 13th European Congress on Catalysis (EUROPACAT 2017), Florence, Italy, 2017.8.28.
4. T. Ishida, "Supported Gold Nanoparticle-Catalyzed Coupling Reactions", Dalian Institute of Chemical Physics-Tokyo Metropolitan University (DICP-TMU) Joint Symposium on Gold Catalysis Research, Dalian, China, 2017.9.29.
5. T. Murayama, “Gold nanoparticulate catalysts deposited on solid acid and their application for oxidation reactions”, Dalian Institute of Chemical Physics-Tokyo Metropolitan University (DICP-TMU) Joint Symposium on Gold Catalysis Research, Dalian, China, 2017.9.29.
6. J. Nishigaki, “Interconversion of NADH and NAD^+ by gold cluster catalysts: regeneration of active coenzymes in dehydrogenase catalytic process”, Dalian Institute of Chemical Physics-Tokyo Metropolitan University (DICP-TMU) Joint Symposium on Gold Catalysis Research, Dalian, China, 2017.9.29.
7. T. Fujita, K. Shibamoto, M. Haruta, “Effects of calcination temperature and atmosphere on Au/ZnO catalyst for CO oxidation”, Dalian Institute of Chemical Physics-Tokyo Metropolitan University (DICP-TMU) Joint Symposium on Gold Catalysis Research, Dalian, China, 2017.9.29.
8. A. Taketoshi, T. Ishida, M. Haruta, “Preparation of Gold Clusters on Metal Oxides by Deposition-Precipitaion with Microwave Drying”, Dalian Institute of Chemical Physics-Tokyo Metropolitan University (DICP-TMU) Joint Symposium on Gold Catalysis Research, Dalian, China, 2017.9.29.
9. R. Sodenaga, T. Ishida, M. Haruta, "Supported gold-catalyzed transfer vinylation of carboxylic acid", Dalian Institute of Chemical Physics-Tokyo Metropolitan University (DICP-TMU) Joint Symposium on Gold Catalysis Research, Dalian, China, 2017.9.29.
10. T. Murayama, “Nanoparticulate gold catalyst deposited on polyoxometalate”, Workshop Cardiff & TMU, Cardiff University, Cardiff, UK, 2018.2.5.
11. A. Taketoshi, “Oxidative Esterification of Aliphatic Aldehydes Catalyzed by Gold Nanoparticles in Bach and Continuous Flow Reactors”, Workshop Cardiff & TMU, Cardiff University, Cardiff, UK, 2018.2.5.
12. T. Ishida, “Supported Gold Nanoparticle Catalysts for C-H Bond Transformation”, Workshop Cardiff & TMU, Cardiff University, Cardiff, UK, 2018.2.5.

＊**International (Poster)**

1. T. Ishida, R. Sodenaga, T. Honma, M. Haruta, "Transfer Vinylation Catalyzed by Supported Gold Catalysts", The 2nd International Symposium on Hydrogen Energy–based Society, Tokyo Metropolitan University, 2017.11.21

＊**Domestic (oral)**

See the annual report in Japanese (13 articles)

＊**Domestic (poster)**

See the annual report in Japanese (8 articles)

■**Awards**

1. T. Ishida, The 5th Seki Memorial Award, “Development of Organic Reactions by Supported Metal Cluster catalysts”, Seki Memorial Foundation for Science, 2017.11.8.

■**Others**

1. Ultra-efficient removal of carbon monoxide using gold nanoparticles on a molecular support ~New method and mechanism for state-of-the-art gas purification~, TOKYO METROPOLITAN UNIVERSITY, EurelAlert!, PUBLIC RELEASE: 9-FEB-2018.

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Doctor's course -7
Master's course -15
Bachelor 4 -9

■Outlines of the Research

1. Research on Rechargeable batteries

Kiyoshi KANAMURA, Hirokazu MUNAKATA

Research and development on next generation rechargeable batteries with high energy density and excellent safety were promoted in order to realize a sustainable society based on high utilization of energy. We successfully improved the electrochemcial performance of all solid state rechargeable batteries using oxide-based solide electrolytes by using composite electrode including ionic liquid and solid electrolyte powder (Fig. 1). A practical solid electrolyte system with high flexibility composing of inorganic and organic electrolyte materials (Fig. 2) was also prepared.

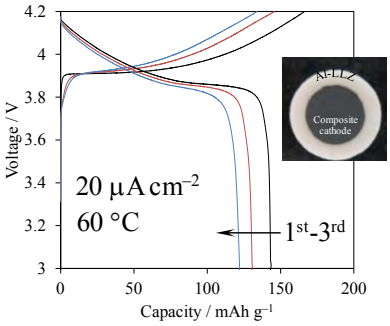

Fig. 1 Charge-discharge curves of the all solid state battery with a composite cathode prepared.

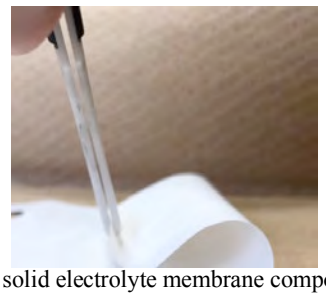

Fig.2 A flexible solid electrolyte membrane composed of inorganic and organic electrolyte materials.

2. Research on Fuel cells

Kiyoshi KANAMURA, Hirokazu MUNAKATA

The development of a new fuel cell system that works at intermediate temperatures over 100 °C under non-humidified conditions was promoted. In this fuel cell, a heat energy produced from fuel cell is recovered by reforming system, leading to high energy conversion efficiency. It is found that the mixture of phosphoric acid / ionic liquid works as highly proton-conductive stable electrolyte at intermediate temperatures. The fuel cell operated at 180 ° C without humidification (Fig. 3) by using this mixed electrolyte.

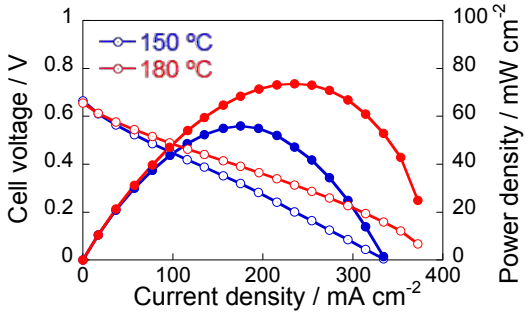

Fig. 3 Fuel cell operation at intermediate temperatures without humidification.

3. Research on optical and electrical properties of inorganic oxides and related materials

Koichi KAJIHARA

Fundamental properties of inorganic oxides, in particular, their optical and electrical properties, were studied to fully utilize the functionalities of oxides. In this FY we focused on the studies on solid electrolytes. We developed a facile method to obtain glass-ceramics of lithium boracite $Li_4B_7O_{12}Cl$. In addition, we found for the first time that the boron sites of this compound can be replaced by other metal ions and discovered a new compound $Li_4B_4M_3O_{12}Cl$(M = Al, Ga), exhibiting the highest Li^+ ion conductivity (~10^{-5} S cm^{-1} at room temperature) among known lithium boracites (Fig. 4). The compound with M = Al was found to be stable to contact with Li metal and is applicable to all-solid-state rechargeable lithium batteries. We also succeeded the high-temperature measurements of dc conductivity and transference number of Mg^{2+}-ion-conducting ceramic $Mg_{0.5-x}(Zr_{1-x}Nb_x)_2(PO_4)_3$ (x = 0.15) using Mg electrodes in vacuum, and demonstrated the dc conduction of Mg^{2+} ions in this compound directly (Fig. 5).

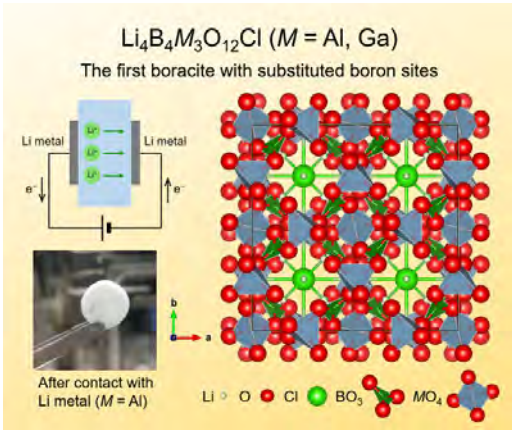

Fig. 4 Crystal structure of the newly discovered lithium-ion-conducting compound $Li_4B_4M_3O_{12}Cl$ (M = Al, Ga) and photograph of a glass-ceramic sample of M = Al after contact with Li metal.

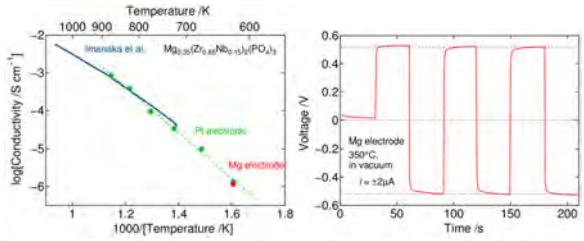

Fig. 5 Arrhenisus plot of ac conductivity of $Mg_{0.5-x}(Zr_{1-x}Nb_x)_2(PO_4)_3$ (x = 0.15) pellets measured with blocking Pt and non-blocking Mg electodes (left) and dc polarization profile of the pellet measured with Mg electrodes at 350°C (right).

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1. Yuta Maeyoshi, Shohei Miyamoto, Hirokazu Munakata, Kiyoshi Kanamura, Enhanced cycle stability of $LiCoPO_4$ by using three-dimensionally ordered macroporous polyimide separator, J. Power Sources 350, 103–108 (2017)
2. Ryo MATSUOKA, Shigeo AOYAGI, Naoshi MATSUMOTO, Masaaki MATSUDAIRA, Yasufumi TAKAHASHI, Akichika KUMATANI, Hiroki IDA, Hirokazu MUNAKATA, Katsuhiko IIDA, Hitoshi SHIKU, Kiyoshi KANAMURA, Tomokazu MATSUE, Advanced Scanning Electrochemical Microscope System for High-Resolution imaging and Electrochemical Applications, Electrochemistry, 85, 316-326 (2017).
3. Sunghyun Lim, Ji-Hyun Kim, Yuto Yamada, Hirokazu Munakata, Young-Seak Lee, Sung-Soo Kim, Kiyoshi Kanamura, Improvement of rate capability by graphite foam anode for Li secondary batteries, J. Power Sources 355, 164-170 (2017).
4. Enhanced Electrochemical Performance of $LiMn_{0.75}Fe_{0.25}PO_4$ Nanoplates from Multiple Interface Modification by Using Fluorine-Doped Carbon Coating, ACS Sustainable Chem. Eng., 5, 4637–4644 (2017).
5. Kei Nishikawa, Nobuyuki Zettsu, Katsuya Teshima, Kiyoshi Kanamura, Intrinsic electrochemical characteristics of one $LiNi_{0.5}Mn_{1.5}O_4$ spinel particle, J. Electroanal. Chem., 799, 468-472 (2017).
6. Jungo Wakasugi, Hirokazu Munakata, Kiyoshi Kanamura, Improvement of sintering of $Li_{6.25}Al_{0.25}La_3Zr_2O_{12}$ by using pre-heat treatment, Solid State Ionics, 309, 9–14 (2017).
7. Yanqing Wang, Zengqi Zhang, Masaki Haibara, Deye Sun, Xiaodi Ma, Yongcheng Jin, Hirokazu Munakata, Kiyoshi Kanamura, Reduced Polysulfide Shuttle Effect by Using Polyimide Separators with Ionic Liquid-based Electrolytes in Lithium-Sulfur Battery, Electrochim. Acta, 255, 109-117 (2017).
8. Yuta Maeyoshi, Shohei Miyamoto, Hirokazu Munakata, Kiyoshi Kanamura, Effect of conductive carbon additives on electrochemical performance of $LiCoPO_4$, J. Power Sources, 376, 18-25 (2018).
9. Naoto Tezuka, Yuta Okawa, Koichi Kajihara, Kiyoshi. Kanamura, Synthesis and characterization of lithium-ion-conductive glassceramics of lithium chloroboracite $Li_{4+x}B_7O_{12+x/2}Cl$ (x = 0–1), J. Ceram. Soc. Jpn. 125, 348-352 (2017)
10. Koichi Kajihara, Hayato Nagano, Takaoki Tsujita, H.irokazu Munakata, Kiyoshi Kanamura, High-temperature conductivity measurements of magnesium-ion-conducting solid oxide $Mg_{0.5-x}(Zr_{1-x}Nb_x)_2(PO_4)_3$ (x = 0.15) using Mg metal electrode, J. Electrochem. Soc. 164, A2183-A2185 (2017)
11. Koichi Kajihara, Naoto Tezuka, Mao Shoji, Jungo Wakasugi, Hirokazu Munakata, Kiyoshi Kanamura, $Li_4B_4M_3O_{12}Cl$ (M = Al, Ga): an electrochemically stable, lithium-ion-conducting cubic boracite with substituted boron sites, Bull. Chem. Soc. Jpn. 90, 1279-1286 (2017)
12. Linards Skuja, Koichi Kajihara, Krisjanis Smits, Kalvis Alps, Andrejs Silins, Janis Teteris, Luminescence properties of chlorine molecules in glassy SiO_2 and optical fibre waveguides, Proc. Est. Acad. Sci 66, 455-461 (2017)

■Books

See the annual report in Japanese (3 articles)

■Invited Lectures

1. Kiyoshi Kanamura, Interfacial Control of All Solid State Battery with Li Metal Anode, LLZAl Electrolyte and $LiMO_2$ Cathode, PACRIM12, May, 2017, Waikoloa, Hawaii, USA
2. Kiyoshi Kanamura, Masaki Haibara, Naohiro Kobori, and Hirokazu Munakata, Interfacial Behavior of Li Metal Anode in Nonaqueous Electrolytes Under Controlled Current Distribution, 2017 International Workshop on Electrified Interfaces for Energy Conversions, May, 2017, Shonan Village Center, Kanagawa, Japan
3. Koichi Kajihara, Tatsuya Mori, Kiyoshi Kanamura, Yoshitake Toda, Hidenori Hiramatsu, and Hideo Hosono, Synthesis, structure, and properties of indium-based ultraviolet-transparent electroconductive oxyfluoride InOF, STAC10, Aug., 2017, Mielparque Yokohama, Kanagawa, Japan
4. Kanamura Kiyoshi, Kozuka Kyoko, Shoji Mao, Kimura Takeshi, Munakata Hirokazu, Preparation of All solid State Battery by Aero Sol Deposition Method, INESS2017, Aug., 2017, Astana, Kazakhstan
5. Munakata Hirokazu, Kikuchi Shojiro, Ionic Liquid/Phosphoric Acid Mixed Electrolyte for Non-humidified Intermediate Temperature Fuel Cells, INESS2017, Aug., 2017, Astana, Kazakhstan
6. Kiyoshi KANAMURA, Kyoko KOZUKA, Takeshi KIMURA, Mao SHOUJI, Hirokazu MUNAKATA, All solid state battery with Li metal anode and oxide cathode prepared by aero-sol deposition process, IUMRS-ICAM2017, Aug., 2017, Kyoto University, Kyoto, Japan
7. Kiyoshi Kanamura, Dendrite Suppression of Li Metal in Various, ACEPS9, Aug., 2017, HICO, Gyeongju, Korea
8. Kiyoshi Kanamura, Takeshi Kimura, Kyoko Kozuka, Mao Shoji, Hirokazu Munakata, Interface Formation of All-solid-state Rechargeable Lithium Batteries, 1st World Conference on Lithium Garnets, Competitors and Beyond for Advanced Batteries, Sep., 2017, Hotel Ocean Spray, Pondicherry, India
9. Kiyoshi Kanamura, Fabrication of All-Solid-State Battery with Aero Sol Deposition Process for Cathode Layer, 2017 MRS Fall Meeting & Exhibit, Nov., 2017, Boston, USA
10. Hirokazu Munakata, Jungo Wakasugi, Kyoko Kozuka, Takeshi Kimura, Mao Shoji, Kiyoshi Kanamura, Electrode Fabrication for All-solid-state Rechargeable Lithium Batteries using $Li_{6.25}Al_{0.25}La_3Zr_2O_{12}$ Solid Electrolyte, ICACC2018, Jan., 2018, Daytona Beach, Fla. USA

■Academic Meeting

＊International

1. Linards Skuja, Koichi Kajihara, Krisjanis Smits, Andrejs Silins, Janis Teteris, Luminescence properties of chlorine molecules in glassy SiO_2 and optical fiber waveguides, International Conference 'Functioanal Materials and Nanotechnologies 2017 (FM&NT-2017), Apr., 2017, Tartu, Estonia
2. Hasna Puthen Peediyakkal, Shojiro Kikuchi, Yu Jie, Hirokazu Munakata, Kiyoshi Kanamura, Electrochemical Oxygen Reduction on Nitrogen Doped Graphene in Ionic Liquid at Intermediate Temperatures, 2017 International Workshop on Electrified Interfaces for Energy Conversions, May, 2017, Shonan Village Center, Kanagawa, Japan

3. Fumihiro SAGANE, Kenta OGI, Akinori KONNO, Kiyoshi KANAMURA, Effect of the cyclic ethers on the reversible Mg plating/stripping reaction for Mg batteries, IUMRS-ICAM2017, Aug., 2017, Kyoto University, Kyoto
4. Kei NISHIKAWA, Kiyoshi KANAMURA, Electrodeposition of Li metal from various electrolytes, IUMRS-ICAM2017, Aug., 2017, Kyoto University, Kyoto
5. Hirokazu Munakata, Jungo Wakasugi, Kiyoshi Kanamura, Investigation of sintering process of aluminum-doped lithium lanthanum zirconate for dense pellet fabrication, 1st World Conference on Lithium Garnets, Competitors and Beyond for Advanced Batteries, Sep., 2017, Hotel Ocean Spray, Pondicherry, India
6. Mao Shoji, Hirokazu Munakata, Kiyoshi Kanamura, Interface formation between $LiCoO_2$ and $Li_7La_3Zr_2O_{12}$ using solvate ionic liquids for all-solid-state batteries, 1st World Conference on Lithium Garnets, Competitors and Beyond for Advanced Batteries, Sep., 2017, Hotel Ocean Spray, Pondicherry, India
7. Takeshi Kimura, Mao Shoji, Hirokazu Munakata, Kiyoshi Kanamura, Electrochemical properties of Solid/Liquid Composite-type Electrolyte for Next-Generation Lithium Batteries, 1st World Conference on Lithium Garnets, Competitors and Beyond for Advanced Batteries, Sep., 2017, Hotel Ocean Spray, Pondicherry, India
8. T. Mandai, K. Kanamura, A Key Concept of Utilization of Both Magnesium Chloride and Imide Salts for High Temperature Rechargebale Mg Battery Electrolytes, 232nd ECS meeting, Oct., 2017, National Harbor, USA
9. H. Puthen Peediyakkal, S. Kikuchi, J. Yu, H. Munakata, K. Kanamura, The Electrochemical Activity of Nitrogen Doped Graphene Towards Oxygen Reduction Reaction in Ionic Liquid at Intermediate Temperature, 232nd ECS meeting, Oct., 2017, National Harbor, USA
10. H. Munakata, J. Wakasugi, K. Kanamura, Investigation of Thermal Compatibility of Various Cathode Materials with $Li_{6.25}Al_{0.25}La_3Zr_2O_{12}$ Solid Electrolyte for All-Solid-State Rechargeable Lithium Batteries, 232nd ECS meeting, Oct., 2017, National Harbor, USA
11. H. Yamashita, T. Ogami, K. Kanamura, Enhanced Electrochemical Performance of $Li_2Mn_{0.25}Co_{0.75}SiO_4$/C Cathode Materials for Li-Ion Batteries through Reduced Graphene Oxide Addition, 232nd ECS meeting, Oct., 2017, National Harbor, USA
12. K. Nishikawa, K. Kanamura, Electrodeposition of Li Metal Onto a Micro-Electrode in Various Electrolytes, 232nd ECS meeting, Oct., 2017, National Harbor, USA
13. J. Yu, S. Kikuchi, H. P. Peediyakkal, H. Munakata, K. Kanamura, Diethylmethylammonium Trifluoromethanesulfonate / Phosphoric Acid Mixture As Electrolyte for Non-Humidified Intermediate Temperature Fuel Cells, 232nd ECS meeting, Oct., 2017, National Harbor, USA

＊Domestic

See the annual report in Japanese (45 articles)

■Patents

See the annual report in Japanese (1 patent)

■Awards

1. BCSJ Award (vol. 90, no. 12), Koichi Kajihara, Naoto Tezuka, Mao Shoji, Jungo Wakasugi, Hirokazu Munakata, Kiyoshi Kanamura, $Li_4B_4M_3O_{12}Cl$ (M = Al, Ga): an electrochemically stable, lithium-ion-conducting cubic boracite with substituted boron sites, Bull. Chem. Soc. Jpn. 90, 1279-1286 (2017)

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■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.

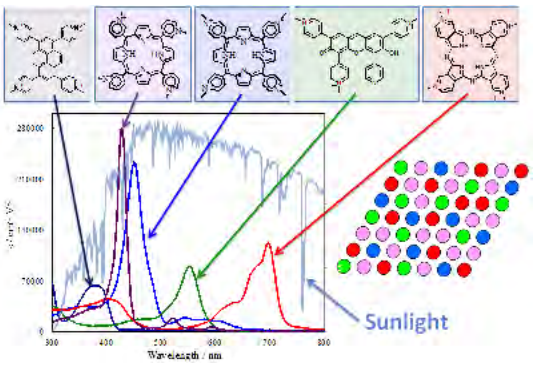

Fig. 1. The effective sunlight harvesting system toward artificial photosynthesis. Dyes with complementary photo-absorption are placed on the clay surface densely without aggregation.

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, 27Al 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.

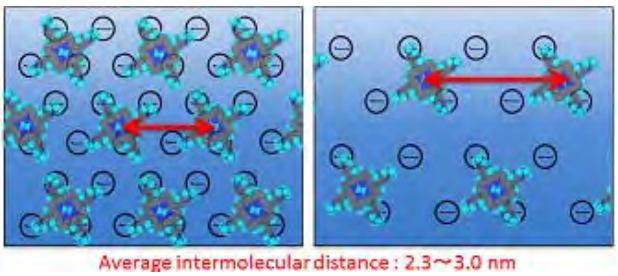

Fig. 2. An example of our methodology to control the adsorption structure of dyes on the clay surface by using a suitable clay species.

3. Surface – Fixation Induced Emission on the nanosheets
Shinsuke TAKAGI, Tetsuya SHIMADA

We investigated the fluorescence enhancement behavior of AIE (Aggregation Induced Emission) – active dyes on the clay nanosheet. Judging from their adsorption observation on the clay in water, the factor for the fluorescence enhancement is turned out not to be AIE, but is to be Surface - Fixation Induced Emission (S - FIE) mechanism. While the effect of AIE depended on the molecular structure of dye in water-dioxane, S - FIE worked even for the dye that has bulky substituent.

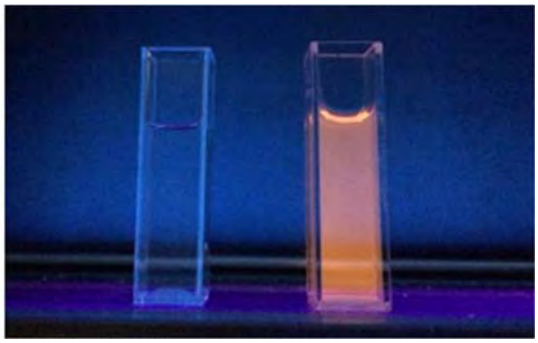

Fig. 3. Surface – Induced Emission on the nanosheets. Left: without nanosheet, Right: with nanosheet..

4. Research on Novel Hybrid Complex of Semiconductor Nano-Sheet and Dye

Shinsuke TAKAGI, Tetsuya SHIMADA

A semiconductor nano-sheet was focused as our new research target in addition to the "insulator" clay nano-sheet. We expected we effectively extend our distinctive research about clay-dye hybridization methodology in order to create new materials with good electron transfer property for artificial photosynthesis system. We synthesized a novel TiO_2 nano-sheet (TNS) and characterized it in detail. We observed adsorption behavior of porphyrin dyes on the TNS and photochemical interaction between the dyes and the TNS.

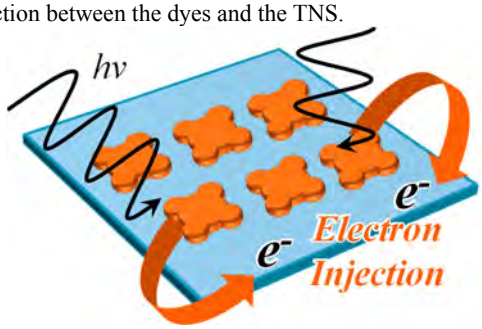

Fig. 4. Electron injection from Dye to semiconductor nanosheet.

■Papers with Peer Review

1. Energy Transfer among Three Dye Components in a Nanosheet-Dye Complex: An Approach To Evaluating the Performance of a Light-Harvesting System, Y. Ohtani, S. Kawaguchi, T. Shimada, S. Takagi, *J. Phys. Chem. C*, **121**, 2052-2058 (2017).
2. "Size-Matching Effect" in Cationic Porphyrin-Titania Nanosheet Complex, A. Sonotani, T. Shimada, S. Takagi, *Chem. Lett.*, **46**, 499-501 (2017).
3. Trapping of excess energy in a nano-layered microenvironment to promote chemical reactions, V. Ramakrishnan, Y. Nabetani, D. Yamamoto, T. Shimada, H. Tachibana, H. Inoue, *Phys. Chem. Chem. Phys.*, **19**, 4734-4740 (2017).
4. Photoinduced electron transfer in layer-by-layer thin solid films containing cobalt oxide nanosheets, porphyrin, and methylviologen, R. Sasai, Y. Kato, W. Soontornchaiyakul, H. Usami, A. Masumori, W. Norimatsu, T. Fujimura, S. Takagi, *Phys. Chem. Chem. Phys.*, **19**, 5611-5616 (2017).
5. Unique Fluorescence Behavior of Dyes on the Clay Minerals Surface: Surface Fixation Induced Emission (S-FIE), D. Tokieda, T. Tsukamoto, Y. Ishida, H. Ichihara, T. Shimada, S. Takagi, *J. Photoch. Photobio. A*, **339**, 67–79 (2017).
6. Light Energy Accumulation from Pyrene Derivative to Tris(bipyridine)ruthenium on Clay Surface, D. Morimoto, H. Yoshida, K. Sato, K. Saito, M. Yagi, S. Takagi, T. Yui, *Langmuir*, **33**, 3680–3684 (2017).
7. Highly Selective Photochemical Epoxidation of Cyclohexene Sensitized by Ru(II) Porphyrin-Clay Hybrid Catalyst, D. Tatsumi, T. Tsukamoto, R. Honna, S. Hoshino, T. Shimada, S. Takagi, *Chem. Lett.*, **46**, 1311-1314 (2017).
8. Photoluminescence by Intercalation of a Fluorescent β-Diketone Dye into a Layered Silicate, M. Hirose, F. Ito, T. Shimada, S. Takagi, R. Sasai, T. Okada, *Langmuir*, **33**, 13515–13521 (2017).
9. Adosorption And Photochemical Behavior Of Mono-Cationic Porphyrin Onto Synthetic Saponite, S. Wakayama, S. Takagi, T. Shimada, *Clay Science*, **20**, 1-3 (2017).
10. Characterization of Dispersed Titania Nanosheet under Aqueous Conditions and its Complex Formation Behavior with Cationic Porphyrin, K. Sano, A. Sonotani, D. Tatsumi, Y. Ohtani, T. Shimada, S. Takagi, *J. Photoch. Photobio. A*, **353**, 597-601 (2018).
11. Active Species Transfer-Type Artificial Light Harvesting System in the Nanosheet – Dye Complexes: Utilization of Longer Wavelength Region of Sunlight, S. Suzuki, D. Tatsumi, T. Tsukamoto, R. Honna, T. Shimada, H. Inoue, S. Takagi, *Tetrahedron Lett.*, *in press*.
12. Elucidation of the Adsorption Distribution of Cationic Porphyrin on the Inorganic Surface by Energy Transfer as a Molecular Ruler, A. Nakayama, J. Mizuno, Y. Ohtani, T. Shimada, S. Takagi, *J. Phys. Chem. C*, *in press*.
13. Fluorescence Enhancement Behavior of Hemicyanine Derivatives on the Clay Nanosheets: Aggregation Induced Emission (AIE) vs. Surface - Fixation Induced Emission (S-FIE), N. Kudo, T. Tsukamoto, D. Tokieda, T. Shimada, S. Takagi, *Chem. Lett.* in press.

■Books

1. Inorganic Nanosheets and Nanosheet-Based Materials (Chapter 1. &14.), S. Takagi, Springer (2017).

+2 articles in Japanese (See the annual report in Japanese)

■Invited Lectures

1. PHOTOCHEMICAL EPOXIDATION WITH LIGHT HARVESTING FUNCTIONALITY ON THE INORGANIC SURFACES, S. Takagi, 2017 International Conference on Artificial Photosynthesis (ICARP2017).
2. Environment-responsive materials composed by dyes and layered compounds, S. Takagi, The 1st International Workshop on Chromogenic Materials and Devices.
3. Dream of artificial photosynthesis, S. Takagi, Third FoS Club Meeting.
4. Unique absorption and emission behavior of layered materials – dyes complexes in special session (Color Materials Science: Coloration Principles and Stimuli-Responsivity), S. Takagi, The 98th CSJ Annual Meeting.
5. Unique reaction field provided by two-dimenssional materials in special session (Next-generation photofunctional materials innovated by dimensional reaction fields), S. Takagi, The 98th CSJ Annual Meeting.

■Academic Meeting

＊International

1. Control of Molecular Assembly Structure on Semiconductor Photocatalyst for Artificial Photosynthesis, K. Sano, A. Sonotani, Y. Ohtani, T. Shimada, S. Takagi, The 2nd International Symposium on Hydrogen Energy–based Society, Tokyo (Japan), November, 2017.

＊Domestic

See the annual report in Japanese (20 articles)

■Patents

1. Patent No. 6183838, S. Takagi, S. Takagi, T. Umemoto, August, 2017.

■Awards

1. Keito SANO, Summer seminar of Forum on Low-dimensional photofunctional Materials, Excellent Presentation Award, September, 2017.
2. Minori MONMA, Summer seminar of Forum on Low-dimensional photofunctional Materials, Excellent Poster Award, September, 2017.
3. Jyunpei HARA, Summer seminar of Forum on Low-dimensional photofunctional Materials, Excellent Poster Award, September, 2017.
4. Keito SANO, The solid and surface photochemistry conference 2017, Excellent oral presentation award, 2017.

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Bachelor 4 -4

■**Outlines of the Research**

1. **Development of Photofunctional Ruthenium Complexes**

Motowo YAMAGUCHI

a) Switching function of ligand photodissociation: A mixed-ligand type ruthenium complex with terpyridine derivative having imidazolyl groups which was reversibly protonated and deprotonated by acid and base has been synthesized and the control of its ligand photodissociation has been examined. The reversible protonation and deprotonation was affirmed, then the ligand photodissociation has been examined in acetone. It was found that the rate of photo-induced dissociation of the complex was considerably inhibited by a factor of a hundred in the presence of base. The high regulation of the rate of the reaction was successfully attained by acid and base. Thus the imidazolyl groups was found to be the useful switch being controllable by the addition of acid and base, and its capability has been improved very much in the control of the rate of ligand dissociation of the complex. Further studies for its application are in progress.

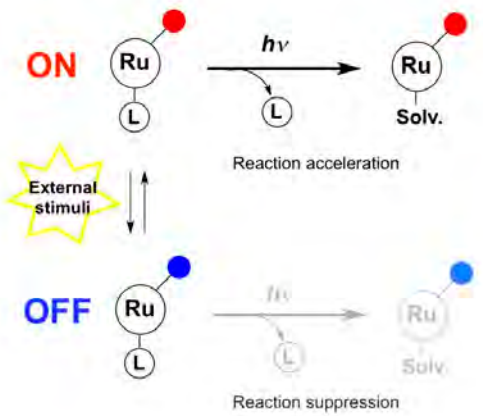

Fig.1 Control of the ligand photodissociation by external stimuli

b) Synthesis of heterodinuclear ruthenium-neodymium complex and its photochemical behavior: New heterodinuclear ruthenium-neodymium complex has been synthesized by using the ruthenium complex having a bridging ligand, bisbenzimidazole, by adding a solution of neodymium complex in acetone. The rate of photoexchange reaction of a MeCN lingand with a solvent molecule in the heterodinuclear complex was slower than that of the deprotonated complex.

c) Pyrazine-bridged macrocyclic tetranuclear complexes and their inclusion behavior: Utilizing the mononuclear ruthenium complex with a tridentate ligand containing a pyrazine moiety as a bridging moiety as the unit, we have found that the macrocyclic tetranuclear complex, molecular square, were selectively obtained by self-assembly. It was found that a rod-like anion, such as a thiocyanide ion or an azide ion, or a spherical ion, such as a halide ion, was included in the cavity of the macrocyclic tetranuclear ruthenium complex, and the inclusion behavior has been examined by ^{1}H NMR and DOSY spectra. The structures of host-guest complex with a halide ion have been examined by DFT calculation. It was found that the host-guest complex with a chloride or a bromide ion has three minima, two in the rim and one in the center of the cavity, while that with an iodide ion has only two in the rim and none in the center since the ion was too large to be included in the cavity.

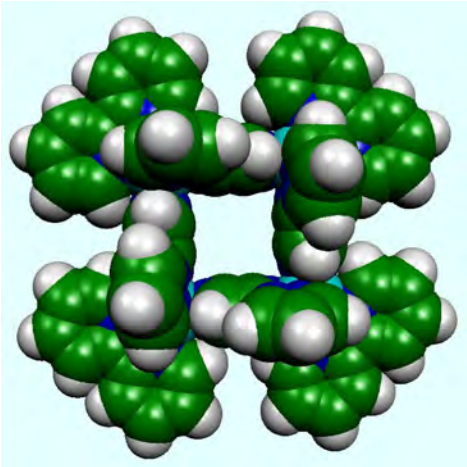

Fig.2 Enegry optimized structure of pyrazine-bridged Ru4 molecular square

2. **Development of Novel Ionic Aggregation-Induced Emission (AIE) Flurophores**

Kiyoshi SATO

Color tunable and stimuli responsible solid-state organic fluorophores attract great attention because of their various applications in bio-imaging dyes, solid-state sensors, and security inks. However, most of typical organic fluorophores showing strong emission in dilute solutions generally exhibit a weak or non-fluorescence in films or in the solid states due to aggregation-caused quenching (ACQ) effect. By contrast, Tang and co-workers reported an opposite phenomenon termed aggregation-induced emission (AIE), which shows weak or non-emission in solutions but strong emission by aggregation. Although a number of AIEgens based on polyaryl-heterocycles have been reported, there are few examples of AIE dyes adopting an ionic heterocyclic core. However, these ionic AIE dyes still have a room for improvement. For instance, the fluorogen of bis(2,4,6-triphenylpyridinio)benzene (BTPPB) yields a photo-bicyclized product during measurements of the fluorescence, the resulting planer polycyclic aromatic cation emits strong fluorescence in solution while forms non-emissive π-stacked aggregates in the solid state. In addition, the AIE activity of BTPPB is even lower than that of typical AIEgens. In this work, we therefore designed a series of new ionic AIE

dyes based on 1,2,4,6-tetraphenylpyridinium cation. The heteroatom-bridged dimers (2-O, 2-S, and 2-NH) show a good photostability, a high AIE activity, and a color tunable emission in the aggregation state.
Initially, in order to verify the intramolecular charge transfer effect on the photostability, the photocyclization of three *para*-OMe substituted 1,2,4,6-tetraphenylpyridinium cations were investigated. In the case of 1-MeOPh, no absorption spectral change was observed after 2h photo-irradiation. The ICT effect also affected to the fluorescence properties. Moreover, 1-MeOPh exhibits higher AIE activity than 2,6-MeOPh and 4-MeOPh derivaties. On the basis of the results above, a series of bridged tetraphenylpyridinium dimers were designed and prepared. The solid-state Φ_f values of the dimers are higher than those of the corresponding monomers. In addition, the heteroatom-bridged dimers, 2-O, 2-S and 2-NH, exhibited good AIE characteristics and their emission wavelengths of the aggregates varied with the electron-donating strength of the heteroatoms.

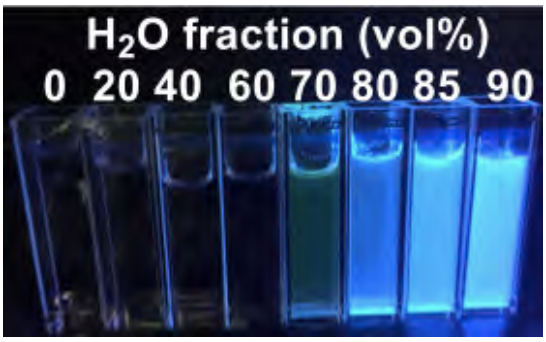

Fig.3 Fluorescence photograph of a heteroatom bridged tetraphenylpyridinium dimer

3. **Synthesis and Properties of Polycyclic Azonia Aromatic Compounds by Multiple Photocyclization**
Kiyoshi SATO
Fused heterocyclic cations having a graphitic-type quaternary nitrogen atom at a bridgehead position of the sp^2-carbon frameworks are expected to exhibit an efficient catalytic activity for water oxidation and their potential use as optical sensors, and electronic devices. The photobiscyclization of 1,2,4,6-tetraarylpyridinium cation is a facile method for the synthesis of the polycyclic heteroaromatic cations. However, in some cases, the photochemical cyclodehydrogenation of substituted 1,2,4,6-tetraphenylpyridiniums stopped at the mono-cyclization stage or completely interrupted due to the electronic influence and/or steric hindrance of the substituents. On the other hand, photobiscyclization of hexaarylpyridinium took place between the 3,4,5-phenyl groups, the reaction site is different from the case of 1,2,4,6-tetraphenylpyridinium. In addition, the photoreaction stopped even though three phenyl groups remained.

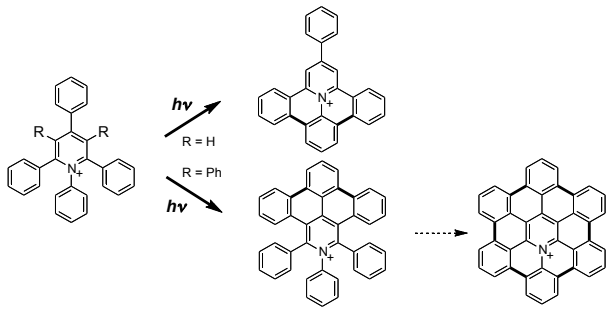

Fig.4 Photobiscyclization of 1,2,4,6-tetraphenylpyridinium and hexaphenylphenylpyridinium cations

Therefore, in this study, in order to elucidate the reactivity and the regioselectivity, the photoreaction of polyarylpyridinium cations was investigated.
The photoreaction of 1,2,3,5,6-pentaphenylpyridinium cation afforded a bis-cyclized photoproduct. The reaction selectively occurs at the 1,2,6-phenyl moiety and no further reaction or other cyclization at different site was observed. To confirm the low reactivity between 2,3- (or 5,6-) phenyl rings, the photoreaction of 1-methyl-2,3,4,5,6-pentaphenylpyridinium and 1-methyl-2,3,5,6-tetraphenylpyridinium cations were investigated. The progress of the reaction between 2,3- (or 5,6-) phenyl rings was very slow. Based on the above findings, the photoreaction of a preliminarily cyclized precursor to the hexabenzocoronene analog is now in progress.

■Papers with Peer Review

1. Dual-mode Cross-coupling on Aromatic Imino Compounds by Dihydridoruthenium Catalysts, D. Hirasawa, Y. Watanabe, T. Yamahara, K. Tanaka, K. Sato, T. Yamagishi, *Molecular Catalysis*, in press (2018)

■Academic Meeting

＊International

1. Motowo YAMAGUCHI, Pyrazine-bridged Macrocyclic Tetranuclear Ruthenium Complex: Synthesis, Inclusion Behavior, and Electrochemical Properties, The 24th International SPACC Symposium, Nov., 2017, Auckland, New Zealand.
2. Wataru MURATA, Kiyoshi SATO, Motowo YAMAGUCHI, Exploring Efficient Metal Complexes as a Catalyst for Hydrogenation and Dehydrogenation, The 2nd International Symposium on Hydrogen Energy–based Society, Nov., 2017, Hachioji, Japan.
3. Ken SEIMIYA, Kiyoshi SATO, Motowo YAMAGUCHI, Application of Bis-Pyridinium Derivatives for a Multi-Electron Anolyte of Aqueous Organic Redox Flow Batteries, The 2nd International Symposium on Hydrogen Energy–based Society, Nov., 2017, Hachioji, Japan.

＊Domestic

4. Motowo YAMAGUCHI, Kento AOSHIMA, Aya HAMAZAKI, and Kiyoshi SATO, Syntheses, Inclusion Behavior, and Electrochemical Properties of Pyrazine-bridged Macrocyclic Tetranuclear Ruthenium Complex, 67th Conference on Coordination Chemistry of Japan, Sept., 2017, Sapporo. (in English)
5. Sakurako TAMAI, Kiyoshi SATO, and Motowo YAMAGUCHI, Synthesis and Property of Ruthenium-neodymium Dinuclear Complex, 67th Conference on Coordination Chemistry of Japan, Sept., 2017, Sapporo. (in Japanese)
6. Kengo NOZAKI, Sachio KIMURA, Motowo YAMAGUCHI, and Kiyoshi SATO, Aggregation-induced Emission Property of Aryl-substituted Pyridinium and Imidazolium Based on Rational Design, 28th Symposium on Physical Organic Chemistry, Sept. 2017, Fukuoka. (in Japanese)
7. Moe TORII, Yusuke IKEDA, Motowo YAMAGUCHI, and Kiyoshi SATO, Synthesis of Diazoniahexabenzoperylene by Multiple Photocyclization, 28th Symposium on Physical Organic Chemistry, Sept. 2017, Fukuoka. (in Japanese)

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Doctor's course -2
Master's course -7
Bachelor 4 -9

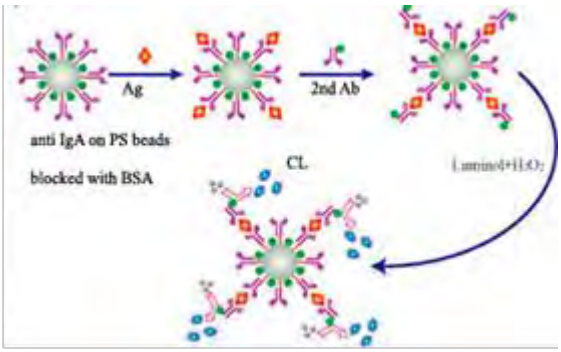
■Outlines of the Research

1. Development of Ultra Small Sample Injection Method Using Inkjet Microchip
   Katsumi UCHIYAMA and Hu-lie ZENG

Ink-jet technology, which enables handling of ultra small liquid samples, has been applied not only to printer but also various fields such as chemistry and material sciences. We have developed ultra small sample introduction method for capilly gas chromatography and capillary electrophoresis. Currently, the technique is applied to on-line sample pre-concentration for capillary electrophoresis and to liquid-liquid extraction.

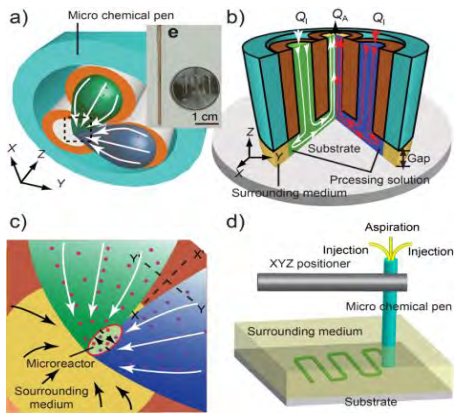
2. Development of Ultra Small Droplet ELISA Using Inkjet Microchip
   Katsumi UCHIYAMA and Hu-lie ZENG

Enzyme linked immunoSorbent assay (ELISA), which is based upon the antigen-antibody reaction, is one of the sensitive determination methods for protein. ELISA is usually carried out with micro titer plate with 96 holes and this enables simultaneous determinations for various samples on the plate. However, in order to complete the whole assay process, it takes much time and sometimes complex procedure is necessary. In order to solve the problem, we have developed ultra small reaction chamber with small droplet formed by ink-jet technology. The system realized acceralation of ELISA assay time and drastic reduction of reagents and sample consumption.



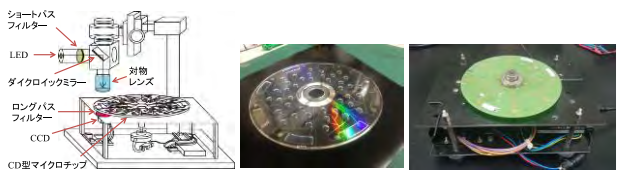
3. Development of Micro Chemical Pen
Katsumi UCHIYAMA

We have developed a new micro chemical pen, which enabled micro chemical modification of the surface of materials. The pen feeded reaction reagent and catalyst onto the material surface that was placed in a liquid and formed micro raction region (sub micrometer to micro meter). Chemical pattern was formed by scanning the pen with x,y stage. This tool will be applied to the arrangement tool for molecular machine and its micro expression of the function, highly functionalization of micro machines and micro total analysis system.



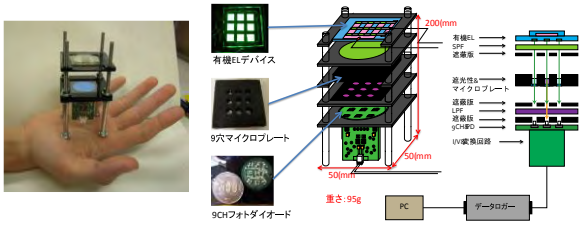
4. Development of Micro Total Analysis System Using a Compact Disk-type Microfluidic Device
Hizuru NAKAJIMA

We have developed a flow-based ELISA system using a microfluidic device. However, many pumps and valves are required for multiple immunoassays, which affect total size of the analytical system. In this study, we developed a solution sending method based on the centrifugal force generated by rotation of a compact disk-type microfluidic device. A novel surface plasmon resonance sensor, a fluorescence detection system and an electrochemical detection system were developed using the compact disk-type microfluidic device. Since pumps and valves are unnecessary, these systems would be useful for on-site analysis, such as environmental monitoring, food safety testing and point-of-care testing.



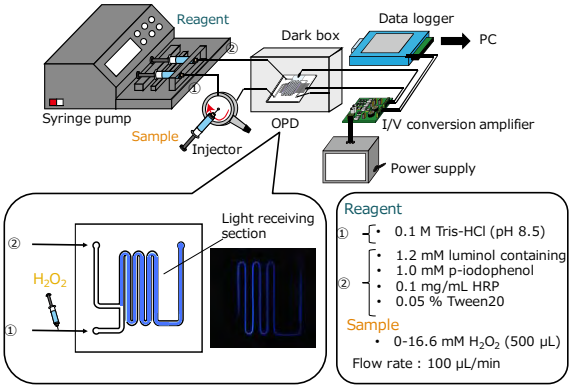
5. Development of Fluorescence Analysis System Using Organic Light Emitting Diodes as Light Source
Hizuru NAKAJIMA

The microfluidic lab-on-a-chip has provided a platform to conduct chemical and biochemical analysis in a miniaturized format. A common detection method for lab-on-a-chip is laser induced fluorescence. However, the method is not suitable for on-site analysis because of the size, weight and cost of the peripheral devices such as lasers and microscopes. We have succeeded in incorporating a light-emitting diode (LED) and an optical fiber into a polymeric microfluidic device in order to miniaturize the total size of the detection system. Recently, organic light emitting diodes (OLEDs) have been very successful for lightweight full-color flat panel displays. The OLEDs have a flat surface, which makes it easy to integrate with microfluidic devices and flexible to fabricate into the required size and shape by photolithography techniques. In this study, we developed a novel portable fluorescence detection system using OLEDs as light source. The system was successfully used in the measurement of IgA in human saliva.



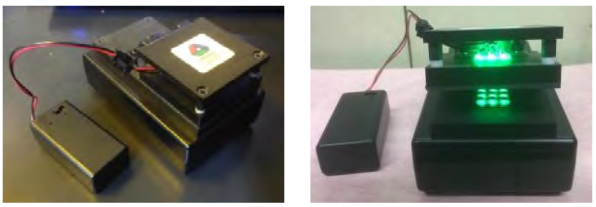
6. Development of Chemiluminescence Analysis System Using Organic Photodiodes as Photo Detector
Hizuru NAKAJIMA

Chemiluminescence method enables high sensitive detection of trace components in environmental and biological samples since the method does not require a light sorce and is not affected by background noise derived from the light sorce. However, it is difficult to apply the chemiluminescence method for on-site analysis since a photomultiplier tube typically used as photo detector in the method is large-size and very expensive. In this study, organic photodiodes (OLEDs) were fabricated on a microfluidic device and then a novel chemiluminescence analysis system was developed using the OLEDs-integrated microfluidic device. The system was successfully used in the determination of hydrogen peroxide based on the enhanced chemiluminescence using luminol.

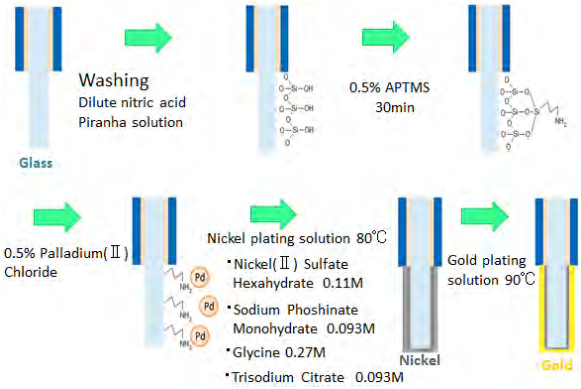


7. Development of Portable ELISA System for Infection Disease Diagnosis
Hizuru NAKAJIMA

Tropical area-specific infection diseases such as dengue fever and chikungunya fever are menaced to society in the world since the viruses, which cause these infection diseases, are easily spread on a global scale by globalization of the economy. In order to minimize the damage of the infection diseases, a rapid diagnostication and a non-proliferation for the viruses are very important. However, these countermeasures for the danger is not sufficient in developing countries because of the economic and technical problems. In this study, we developed a simple, portable and inexpensive ELISA system that can be used for rapid antibody test in the field. The portable ELISA system was successfully used in the antibody tests for measles and rubella viruses.



8. Development of surface plasmon resonance sensor using an optical fiber prepared by electroless displacement gold plating method
Hizuru NAKAJIMA
Optical fiber-type surface plasmon resonance (SPR) sensor has some attractive advantages such as small volume of analytes, miniaturization of senser system and potential capacity for remote sensing. However, it is time-consuming and very costly to form ideal thickness of gold thin film for SPR (ca.50 nm) onto the circular cylinder shaped fiber core, precisely. In this study, a simple and low-cost method for fabricating an optical fiber for SPR sensor was proposed. The method was based on the electroless nickel plating and the subsequent displacement gold plating on the core of the optical fiber. The sensitivity and resolution of the SPR sensor using the fabricated optical fiber was comparable to that of the commercially available SPR sensors. The sensor was successfully used in the measurement of IgA in human saliva.



9. Measurements of VOCs at urban and suburban sites
Shungo KATO
Volatile Organic Compounds (VOCs) were observed at uburban site (Minamiosawa, Tsukuba). Emission sources, contribution to ozone formation of each VOC were estimated.

10. Studies atmospheric pollutants at sub-urban forest area
Shungo KATO
Various trace gas species were observed at suburban forest area (FM-Tama). Vertical distribution of trace gases were observed on the flux tower at forest area. Influence of biogenic VOCs to ozone was discussed.

11. Atmospheric trace species measurements at remote sites
Shungo KATO
Atmospheric carbon monoxide, ozone, and various volatile organic compounds were continuously observed at remote sites: cape Hedo in Okinawa, Moshiri in Hokkaido, Suzu in Ishikawa.

12. Measurements of atmospheric pollutants at mountain sites
Shungo KATO
Carbon monoxide, ozone, and sulferdioxide were observed at summit of Mt. Fuji during summer. There was no influence from local pollution source and typical air at remote site during summer was observed. Plume from volcano was observed at Mt. Fuji. For future winter time measurement without commercial electric power, test measurements of low power gase sensor was demonstrated.

13. Atmospheric trace gas measurements using small gas sensor
Shungo KATO
Atmospheric trace gases was measeured by small gas sensors at urban area and clean remote site at the top of Mt. Fuji. Also, portable system working by battely was constructed.

14. 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 was observed.

13. Application of biochar to stress resistance of proteins
Hidetaka NORITOMI
To reduce greenhouse gas emissions, biochar was prepared from forestry residues, which are carbon neutral, and was used as a protein carrier. We found that biochar imparts high heat stress resistance and organic solvent stress resistance to proteins. This result would be expected to the applications to biosensors, bioreactors, biofuel cells, and so on.

■Papers with Peer Review

1. Sifeng Mao, Yong Zhang, Haifang Li, Hulie Zeng, Jin-Ming Lin, Katsumi Uchiyama
Writing of nanowires via high viscosity-induced nano diffusive layer
Journal of Materials Chemistry C, 2017,5, pp.11666-11671
2. Yong Zhang, Sifeng Mao, Yuma Suzuki, Yumi Tanaka, Masato Kawaguchi, Weifei Zhang, Hulie Zeng, Hizuru Nakajima, Ming Yang, Katsumi Uchiyama
Elaborately programmed nanowires fabricated using a tapered push–pull nozzle system
Chemical Communications, 2018,54, pp.719-722
3. Sifeng Mao, Wanling Zhang, Qiushi Huang, Mashooq Khan, Haifang Li, Katsumi Uchiyama, Jin-Ming Lin
In Situ Scatheless Cell Detachment Reveals Correlation between Adhesion Strength and Viability at Single-Cell Resolution
Angew. Chem. Int. Ed, 2018, 57, pp.236 –240
4. Hulie Zeng, Sifeng Mao, Yong Zhang, Hizuru Nakajima, Katsumi Uchiyama
Reversibly electro-controllable polymer brush for electro-switchable friction
J. Mater. Chem. C, 2017 5, pp5877-5881.
5. Hulie Zeng, Yong Zhang, Hizuru Nakajima, Katsumi Uchiyama
Reversibly electro-switchable poly-allyloxy hydroxypropyl

sulfonate branched brushes and its applications
Sensor. Actuat. B, 2017, 251, pp334-338.

6. Yoshihiro Nakashima1, Hiroshi Tsurumaru, Ramasamy, Sathiyamurthi, Yosuke Sakamoto, Shungo Kato, Yasuhiro Sadanaga, Tomoki Nakayama, Yuzo Miyazaki, Tomoki Mochiduki, Ryuichi Wada, Kazuhide Matsuda1, Yoshizumi Kajii
Ambient measurements and survey of the sources of gaseous glyoxal at suburban site in Tokyo during summer season
J. Jpn. Soc. Atmos. Environ., 2017, Vol.52, No.6, pp.167-176

7. Tomoki Nakayama, Yuuki Kuruma, Yutaka Matsumi, Yu Morino, Kei Sato, Hiroshi Tsurumaru, Sathiyamurthi Ramasamy, Yosuke Sakamoto, Shungo Kato, Yuzo Miyazaki, Tomoki Mochizuki, Kimitaka Kawamura, Yasuhiro Sadanaga, Yoshihiro Nakashima, Kazuhide Matsuda, Yoshizumi Kajii
Missing Ozone-Induced Potential Aerosol Formation at a Suburban Deciduous Forest
Atmospheric Environment, 2017, 171, pp.91-97

8. Chang-Feng Ou-Yang, Chih-Chung Chang, Jia-Lin Wang, Kojiro Shimada, Shiro Hatakeyama, Shungo Kato, Jia-Yang Chiu, Guey-Rong Sheu, Neng-Huei Lin
Characteristics of Summertime Volatile Organic Compounds in the Lower Free Troposphere: Background Measurements at Mt. Fuji
Aerosol and Air Quality Research, 2017, 17(12), pp.3037-3051

9. Hidetaka Noritomi, Jumpei Nishigami, Nobuyuki Endo, Satoru Kato, Katsumi Uchiyama
Influence of water activity on protease adsorbed on biochar in organic solvents
Journal of Materials Science Research, 2017, 6(4), pp. 96-102

■Books

■Invited Lectures

1. Katsumi Uchiyama
Analytical and Chemical Application of Ink-jet
IUPAC International Congress on Analytical Sciences 2017 (ICAS2017), Hainan InternationalConvention & Exhibition Center, 6p-CA-K2

■Academic Meeting

＊International

1. Katsumi Uchiyama
The use of an inkjet injection technique for quantitative on-line electrophoretically mediated micro
Advances in Pharmaceutical Analysis 2017(APA 2017), Wuhan University, China, K14

2. R. Kataoka, M. Momoi, K. Miura, Y. Iwamoto, M. Yabuki, S. Kato
Factors controlling daytime and nighttime new particle formation at the summit of Mt. Fuji, Japan
Asian Aerosol Conference (AAC) 2017, Jeju

3. Shungo Kato, Hiroshi Okochi, Kazuhiko Miura
CO and O3 observation at the summit of Mt. Fuji during summer
2017 Symposium on Atmospheric Chemistry and Physics at Mountain Sites, Gotemba

4. Yukiko Dokiya, Shiro Hatakeyama, Kazuhiko Miura, Hiroshi Okochi, Masashi Kamogawa, Naoki Kaneyasu, Yoko Katayama, Kazuya Sasaki, Shungo Kato, Yukiya Minami, Hiroshi Kobayashi
Ten years research at Mount Fuji research station
2017 Symposium on Atmospheric Chemistry and Physics at Mountain Sites, Gotemba

5. K. Shimada, C. F. Ou-Yang, S. Kato, N. H. Lin1, C. K. Chan, Y. P. Kim, and S. Hatakeyama
Aerosol chemistry in summer at the top of Mt. Fuji
2017 Symposium on Atmospheric Chemistry and Physics at Mountain Sites, Gotemba

6. Ryota Kataoka, Kazuhiko Miura, Masahiro Momoi, Yoko Iwamoto, Masanori Yabuki, Katsuhiro Nagano, Shungo Kato, Hiroshi Kobayashi, Hiroshi Hayami, Hiroshi Okochi
Properties of new particle formation at the summit of Mt. Fuji, Japan - Measured results during summer from 2006 to 2016 ?
2017 Symposium on Atmospheric Chemistry and Physics at Mountain Sites, Gotemba

7. Yosuke Miyauchi, Hiroshi Okochi, Kojiro Shimada, Naoya Katsumi, Yukiya Minami, Hiroshi Kobayashi, Kazuhiko Miura, Shungo Kato, Masaki Takeuchi, Kei Toda, Shinichi Yonemochi
Observation of acidic gases and aerosols in the upper atmospheric boundary layer and in the free troposphere on Mt. Fuji (2)
2017 Symposium on Atmospheric Chemistry and Physics at Mountain Sites, Gotemba

8. Tatsuya Yamaji, Hiroshi Okochi, Satoshi Ogawa, Naoya Katsumi, Kojiro Shimada, Hiroshi Kobayashi, Yukiya Minami, Kazuhiko Miura, Shungo Kato, Shin-ichi Yonemochi, Natsumi Umezawa, Kiyoshi Nojiri, and Kei Toda
Observation of gaseous mercury at the top and the foot of Mt. Fuji
2017 Symposium on Atmospheric Chemistry and Physics at Mountain Sites, Gotemba

9. Ryuichi Wada, Yasuhiro Sadanaga, Shungo Kato, Naoya Katsumi, Hiroshi Okochi, Yoko Iwamoto, Kazuhiko, Miura, Hiroshi Kobayashi, Hitoshi Kamogawa, Jun Matsumoto, Seiichiro Yonemura
NOy measurements at the top of Mt. Fuji
2017 Symposium on Atmospheric Chemistry and Physics at Mountain Sites, Gotemba

10. Shinji Muramoto, Indra Chandra, Yayoi Inomata, Hidenori Higashi, Yoshio Otani, Takafumi Seto, Kazuhiko Miura, Yoko Iwamoto, Shungo Kato
Measurement of particle size distribution of nanoparticles at summit of Mt. Fuji
2017 Symposium on Atmospheric Chemistry and Physics at Mountain Sites, Gotemba

11. Megumi Nakamura, Hiroshi Okochi, Kojiro Shimada, Naoya Katsumi, Yukiya Minami, Hiroshi Kobayashi, Kazuhiko Miura, Shungo Kato
Observation of cloud water chemistry in the free troposphere and the atmospheric boundary layer on Mt. Fuji (4)
2017 Symposium on Atmospheric Chemistry and Physics at Mountain Sites, Gotemba

12. ○Hidetaka Noritomi, Jumpei Nishigami, Nobuyuki Endo, Satoru Kato, Katsumi Uchiyama
Effect of water activity on enzymes adsorbed on biomass charcoal in organic media
Third International Conference on Science, Engineering &

Environment (SEE-USQ 2017), University of Southern Queensland, Brisbane, Australia, 3600

13. Miyu Nakajima, Atsushi Shoji, Kenji Morita, Kazuhiro Morioka, Akio Yanagida, Akihide Hemmi, Hulie Zeng, Shungo Kato, Katsumi Uchiyama, Hizuru Nakajima
Development of surface plasmon resonance sensor using an optical fiber prepared by electroless displacement gold plating method
PITTCON2018, Orlando, Florida , USA, 660-21P

＊Domestic

See the annual report in Japanese (27articles)

■Awards

1. Moeko Osashima (Master's course 1years)
Royal Society of Chemistry Analyst Poster Prize
"Development of fluorescence detection system for on-site analysis using pipette tips"
Proc. of the 66th annual meeting of the Japan Society for Analytical Chemistry (Tokyo University of Science) (in Japanese)

2. Hulie Zeng, Leading Scientist, Graduate School of Urban Environmental Sciences,Tokyo Metropolitan University

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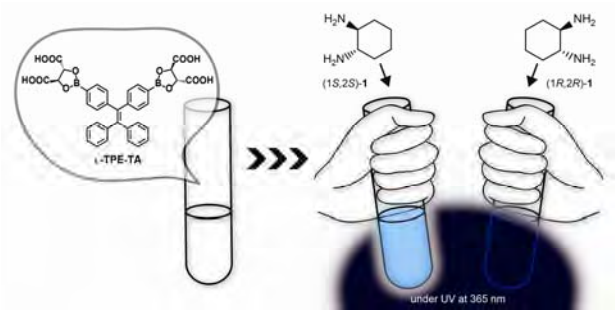
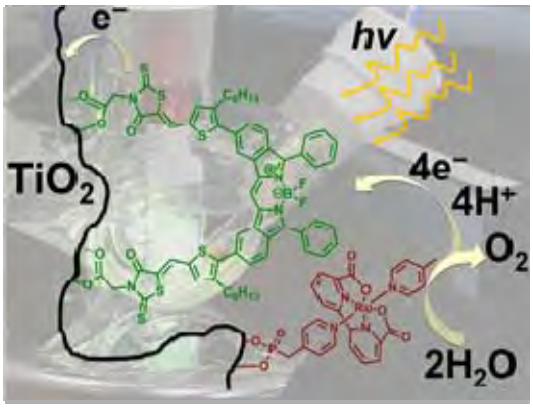
Doctor's course -3
Master's course -13
Bachelor 4 -7

■Outlines of the Research

1. Synthesis of Tetraphenylethylene-Containing Boronate and their Self-Assembly for Chiral Sensing
Name: Yuji Kubo
There has been growing interest in π-conjugated molecules with aggregation-induced emission (AIE) capability, which have prompted chemists to develop new luminescent systems in materials science. To develop hierarchical supramolecules based on boronate esterification, dehydration of di(boronic acid)-appended tetraphenylethylene with tartaric acid was investigated for chiral sensing.



2. Visible Light-induced Water Splitting with Photosensitizing Dye
Name: Yuji Kubo and J. Yan Mulyana
There is an urgent need for creating new energy materials capable of producing hydrogen fuel from water as an alternative to the use of fossil fuels. Our research is concerned with creating bio-inspired energy materials, namely photo electrochemical (PEC) cells, which are capable of harvesting light energy to drive the water splitting process. The construction of the devices involves the synthesis of organic and inorganic materials, which can be assembled with appropriate semiconductors such as titanium oxide (TiO_2) and indium tin oxide (ITO) nanoparticles.



3. Synthesis of Dyes Applicable to Dye-Sensitized Solar Cells
Name: Yuji Kubo
Due to our interest in the development of functional dyes that can absorb longer wavelength of radiations, synthesis and characterization of π-extended dibenzo-boron-dipyrromethenes (dibenzo-BODIPYs) have been investigated. For the approach, the related sensitizers applicable to dye-sensitized solar cells are worthwhile to be investigated. In this study, dibenzo-BODIPYs with a phenothiazinylcyanoacrylic acid group and rhodamine groups have been newly prepared, respectively.

4. Synthesis of Selenophene-containing Dyes
Name: Yuji Kubo
Selenium is relatively more polarizable and softer than sulfur, due to its size. Although the low oxidation potential leads to electron donating property of selenium-containing π-conjugation to endow it with promising OFET materials, the proposal of emissive compounds with selenium are limited because of the heavy atom effect. On another front, there has been increasing demand for the development of dyes with stable excited triplet states. In this study, selenophene-substituted BODIPY (Se-BDP) has been newly synthesized

5. Construction of Triplet-Triplet Annihilation-Based Upconversion Molecular Systems
Name: Yuji Kubo
Triplet-triplet annihilation-based photon upconversion (TTA-UC) have attracted increasing attentions as promising methods for energy conversion from low-energy excitation to higher energy light because of various applications involving solar cells, photocatalysts, and so on. However, TTA-UC is a highly oxygen sensitive process, resulting in a low efficiency in the presence of oxygen. In this study, a Co complex was used to overcome such difficulty, which is known as an oxygen scavenger. Subsequently, we found that the addition of the Co complex into the solution of Pt(II) porphyrin (PtOEP) as a sensitizer and 9,10-diphenylanthracene (DPA) as an annihilator led to significant quenching of UC emission, whereas phosphorescence emission due to the sensitizer almost remained.

6. Synthesis of a 1-hydroxy-2,3,1-benzodiazaborine-containing π-conjugated system
Name: Yuji Kubo and Ryuhei Nishiyabu
A 1-hydroxy-2,3,1-benzodiazaborine conjugated with 1,8-naphthalimide was synthesized. Its fluorescence was dramatically affected by the nature of the solvent. In particular, the use of DMSO, which has a relatively high donor number, led to a remarkable decrease in the fluorescence intensity, possibly due to intermolecular hydrogen-bonding interactions.

The presence of the hydroxyl group on boron led to a solvent-driven colorimetric response towards anions; high selectivity for fluoride ion over other anions in DMSO, and responded to acetate ion and fluoride ion in THF.

7. A zinc-coordinated boronate dipyrrin as a chemodosimeter toward hydrogen peroxide
Name: Yuji Kubo and Ryuhei Nishiyabu
To develop a chemodosimeter for the visual detection of hydrogen peroxide, a dipyrrin dye with 4-pinacolborylbenzyloxy groups was synthesized. An ethanol solution of the dye was reddish-violet in color. The addition of hydrogen peroxide into the solution induced a remarkable color change from reddish-violet to blue. . For practical applications, the related drop-cast paper strips were fabricated to visually detect hydrogen peroxide vapor.

8. Development of Chemical Modifiers for Surface Functionalization of Polyvinyl Alcohol.
Name: Yuji Kubo and Ryuhei Nishiyabu
Chemical modifiers with boronic acid groups as anchoring groups have been synthesized for the development of material-based chemosensors and 3D cell culture matrix through surface functionalization of PVA sponges.

9. Development of near-infrared absorbing photoelectric conversion devices.
Yuji Kubo
There has been a growing interest in near-infrared (NIR)-absorbing dyes with absorption or emission bands beyond 700 nm due to their potential applications in organic electronics. In this study, naphtho[1,3,2]oxazaborinine-type dibenzo-BODIPYs was newly synthesized and incorporated optoelectric devices. The resultant devices would be applicable to near-infrared absorbing photodetectors.

■Papers with Peer Review

1. Y. Kubo, S. Tobinaga, Y. Ueno, T. Aotake, Hi. Yakushiji, and T. Yamamoto, Near-infrared-absorbing Photodetectors Based on Naphtho[1,3,2]oxazaborinine-type Dibenzo-BODIPY Dyes, *Chem. Lett.*, **2018**, *47*, 300−303. DOI: dorg/10.1246/cl.171061
2. I. Purnama Y. Kubo, J. Y. Mulyana, A robust ruthenium complex with nonyl-substituted bpy ligand for dye-sensitized photoelectrochemical cell application, *Inorg. Chim. Acta*, **2018**, *471*, 467−474. DOI: 10.1016/j.ica.2017.11.052
3. M. Kawai, A. Hoshi, R. Nishiyabu and Y. Kubo, Fluorescent chirality recognition by simple boronate ensembles with aggregation-induced emission capability, *Chem. Commun.*, **2017**, *53*, 10144−10147. DOI: 10.1039/C7CC05784A
4. S. Erten-Ela, Y. Ueno, T. Asaba and Y. Kubo, Synthesis of a dibenzo-BODIPY-incorporating phenothiazine dye as a panchromatic sensitizer for dye-sensitized solar cells, *New. J. Chem.*, **2017**, *41*, 10367−10375. DOI: 10.1039/C7NJ01735A
5. O. Suryani, Y. Higashino, J. Y. Mulyana, M. Kaneko, T. Hoshi, K. Shigaki and Y. Kubo, Near-infrared organic photosensitizer for use in dye-sensitized photoelectrochemical water splitting, *Chem. Commun.*, **2017**, *53*, 6784−6787. DOI: 10.1039/C7CC02730C
6. R. Nishiyabu, S. Iizuka, S. Minegishi, H. Kitagishi, and Y. Kubo, Surface modification of polyvinyl alcohol sponge with functionalized boronic acid to develop porous materials for multicolor emission, chemical sensing and 3D cell culture, *Chem. Commun.*, **2017**, *53*, 3563−3566. DOI: 10.1039/C7CC00490G
7. K. Sakakibara, Y. Takahashi, R. Nishiyabu and Y. Kubo, A Zn^{2+}-coordinated boronate dipyrrin as a chemodosimeter toward hydrogen peroxide, *J. Mater. Chem. C*, **2017**, *5*, 3684−3691. DOI: 10.1039/C7TC00405B (2017 Journal of Materials Chemistry C HOT papers)
8. Y. Satta, R. Nishiyabu, T. D. James and Y. Kubo, A 1-hydroxy-2,3,1-benzodiazaborine-containing π-conjugated system: synthesis, optical properties and solvent-dependent response toward anions, *Tetrahedron*, **2017**, *73*, 2053−2061. DOI: 10.1016/j.tet.2017.02.050
9. Y. Kubo and R. Nishiyabu, White-light emissive materials based on dynamic polymerization in supramolecular chemistry, *Polymer*, **2017**, *128*, 257−275. DOI:10.1016/j.polymer.2016.12.082.

■Invited Lectures

1. Hierarchical supramolecules using boronic acid building blocks, Yuji Kubo, The 4th International Seminar of Chemistry, Bundung (Indonesia), September 29th, 2018 (Plenary lecture).

See the annual report in Japanese for other invited lectures (two presentations).

■Academic Meeting

＊International

1. A near-infrared organic photosensitizer for use in dye sensitized photoelectrochemical water splitting , Okta Suryani, Yuta Higashino, J. Yan Mulyana, Yuji Kubo, Chemistry conference for young scientists, Blankenberge, Belgium, 2018, Feb 21st

＊Domestic

See the annual report in Japanese for other presentations (13 presentations).

1. A near-infrared organic photosensitizer for use in dye sensitized photoelectrochemical water splitting , Okta Suryani, Yuta Higashino, J. Yan Mulyana, Yuji Kubo, 1C03, Annual meeting on photochemistry 2017 , Tohoku University, 2017, Sep 4th
2. A near-infrared organic photosensitizer for use in dye sensitized photoelectrochemical water splitting , Okta Suryani, Yuta Higashino, J. Yan Mulyana, Yuji Kubo, 2P-54, International symposium on novel energy nanomaterials, catalysts and surfaces for future earth, The University of electro-communications, 2017, Oct 29th
3. A new and robust ruthenium photosensitizer for light-induced hydrogen production from water in dye-sensitized photoelectrochemical cells (DSPECs), Indra Purnama, Yuji Kubo, Jacob Yan Mulyana , 2P-55 , International symposium on novel energy nanomaterials, catalysts and surfaces for future earth, The University of electro-communications, 2017, Oct 29th
4. A near-infrared organic photosensitizer for use in dye sensitized photoelectrochemical water splitting , Okta Suryani, Yuta Higashino, J. Yan Mulyana, Yuji Kubo, P-13, The 2nd International symposium on hydrogen energy-based society, Tokyo Metropolitan University, 2017, Nov 21st
5. A new and robust ruthenium photosensitizer for light-induced hydrogen production from water in dye-sensitized photoelectrochemical cells (DSPECs), Indra Purnama, Yuji Kubo, Jacob Yan Mulyana, P-3, The 2nd

International symposium on hydrogen energy-based society, Tokyo Metropolitan University, 2017, Nov 21st

6. Synthesis of a quinoline amide dye with a boronic acid-grafting group and its application to chemosensors, Uji;Pramoto, Yuji Kubo, 1F5-36, The 98th CSJ Annual meeting Nihon University, 2018, March 20th,
7. Photocatalytic hydrogen production using a dibenzo-BODIPY-incorporated phenothiazine as panchromatic photosensitizer, Okta Suryani, Yumi Maeda, J. Yan Mulyana, Yuji Kubo, 3I1-07, The 98th CSJ Annual meeting Nihon University, 2018, Mar 22nd
8. Dynamics of water reduction by dye-sensitized photoelectrochemical cells incoporating ruthenium photosensitizers, Indra Purnama, Yuji Kubo, Jacob Yan Mulyana oral, 2B5-43, The 98th CSJ Annual meeting, Nihon University, 2018, Mar 22nd

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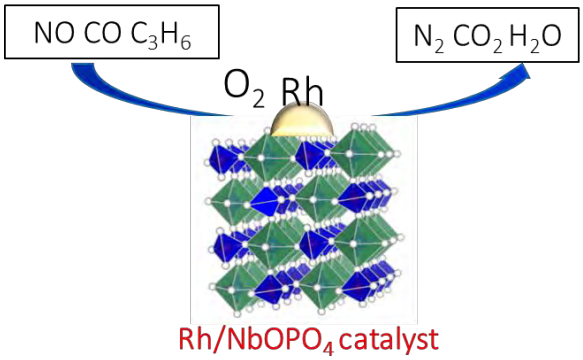
Doctor's course -1
Master's course -15
Bachelor 4 -7

■Outlines of the Research

1. Metal-oxide based catalysts effective for converstion of exhaust gas from vehicles
Tetsuya Shishido, Hiroki Miura

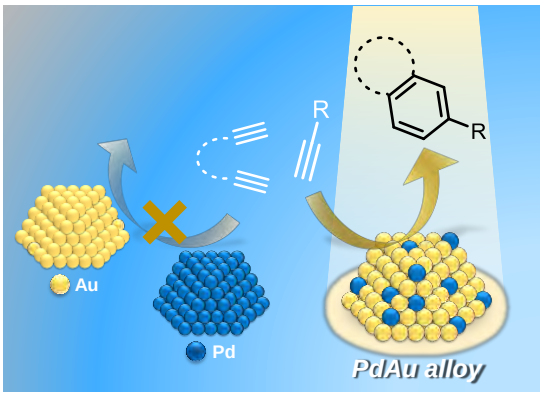
The reduction of the amount of PGM or the development of replaceable materials have been investigated extensively. However, this is still a challenging subject, especially the reduction of NO_x (NO and NO_2) into N_2 without PGM.

We studied catalytic performance of supported Rh catalysts, which possess a high surface area and thermal stability. The catalytic activity was evaluated using test reactions of NO, CO, and C_3H_6 under various simulated exhausts with different air-to-fuel ratios. As a result, $Rh/NbOPO_4$ showed higher catalytic activity than conventional Rh/Al_2O_3 catalyst. Especially, $Rh/NbOPO_4$ exhibited superior NO reduction activity under O2-excess condition (lean condition).



2. Development of supported alloy nanoparticle catalysts effective for [2+2+2] cycloaddition of alkynes
Tetsuya Shishido, Hiroki Miura

Transition metal-catalyzed [2+2+2] cycloaddition of substituted alkynes, which involves the formation of three C-C bonds, is the most elegant, versatile and atom-economical method for constructing polyfunctionalized arenes. Hence, the development of a novel catalytic system with a wide substrate scope as well as substantial environmental compatibility is highly important. In this year, we found that supported PdAu alloy catalysts showed high activity for [2+2+2] cycloaddition of alkynes. Furthermore, detailed structural analyses of the alloy catalysts revealed that the coexistence of Pd species and Au species is indispensable for the efficient cycloaddition over Pd–Au NPs.



3. Green transformation of organic molecules by transition-metal catalysts
Hiroki Miura, Tetsuya Shishido

Selective C-C bond formation by transition-metal catalysts is important method for synthesizing complex organic molecules often found in midicines and functional organic materials. In this year, we investigated ruthenium-catalyzed addition of aromatic acids to aldehydes to give isobenzofuranone derivatives. Under optimized conditions, a series of isobenzofuranones were obtained in good to high yields. Furthermore, we also found that supported Ru catalysts were effective for the title reaction, and the supported catalytsts could be reused for several times without significant loss of activity.

■Papers with Peer Review

1. Hydrosilylation of Allenes over Palladium–Gold Alloy Catalysts: Enhancing Activity and Switching Selectivity by the Incorporation of Palladium into Gold Nanoparticles Miura, H.; Sasaki, S.; Ogawa, R.; Shishido, T. *Eur. J. Org. Chem.* **2018**, DOI:10.1002/ejoc.201800224
2. Dynamic Behavior of Rh Species of Rh/Al_2O_3 Model Catalyst During Three-Way Catalytic Reaction – An Operando XAS Study Asakura, H.; Hosokawa, S.; Ina, T.; Kato, K.; Nitta, K.; Uera, K.; Uruga, T.; Miura, H.; Shishido, T.; Ohyama, J.; Satsuma, A.; Sato, K.; Yamamoto, A.; Hinokuma, S.; Yoshida, H.; Machida, M.; Yamazoe, S.; Tsukuda, T.; Teramura, K.; Tanaka, T. *J. Am. Chem. Soc.* **2018**, *140*, 176-184.
3. Selective Hydrogenolysis of Tetrahydrofurfuryl Alcohol over $Pt/WO_3/ZrO_2$ Catalysts : Effect of WO_3 loading amount on activity Feng, S.; Nagao, A.; Aihara, T.; Miura, H.; Shishido, T. *Catal. Today* **2018**, *303*, 207-212.
4. Concerted Functions of Surface Acid-Base Pairs and Supported Copper Catalysts for Dehydrogenative Synthesis of Esters from Primary Alcohols Miura, H.; Nakahara, K.; Kitajima, T.; Shishido, T. *ACS Omega* **2017**, *2*, 6167-6173.

5. Effect of WO_3 loading on the activity of $Pt/WO_3/Al_2O_3$ catalysts in selective hydrogenolysis of glycerol to 1,3-propanediol Aihara, T.; Kobayashi, H.; Feng, S.; Miura, H.; Shishido, T. *Chem. Lett.* **2017**, *46*, 1497-1500.
6. Highly active and stable Pt-Sn/SBA-15 catalyst prepared by direct reduction for ethylbenzene dehydrogenation: Effects of Sn addition Deng, L.; Arakawa, T.; Ohkubo, T.; Miura, H.; Shishido, T.; Hosokawa, S.; Teramura, K.; Tanaka, T. *Ind. Eng. Chem. Res.* **2017**, *56*, 7160-7172.
7. Strong metal-support interaction between Pt and SiO_2 following high-temperature reduction: a catalytic interface for propane dehydrogenation Deng, L.; Miura, H.; Shishido, T.; Hosokawa, S.; Teramura, K.; Tanaka, T. *Chem. Commun.* **2017**, *53*, 6937-6940.
8. Supported Palladium–Gold Alloy Catalysts for Efficient and Selective Hydrosilylation under Mild Conditions with Isolated Single Palladium Atoms in Alloy Nanoparticles as the Main Active Site Miura, H.; Endo, K.; Ogawa, R.; Shishido, T. *ACS Catal.* **2017**, *7*, 1543−1553.
9. Ruthenium-catalyzed Addition of Aromatic Amides to Internal Alkynes and Subsequent Intramolecular Cyclization for the Atom-Economical Synthesis of Isoindolinones Miura, H.; Terajima, S.; Tsutsui, K.; Shishido, T. *J. Org. Chem.* **2017**, *82*, 1231–1289.

■Invited Lectures

1. 37th annual meeting of Hydrogen Energy Systems Society of Japan, "Approach to realization of low-carbon society based on hydrogen energy in TMU" (invited lecture)」2018/3/1 Nihon University
2. 1st Open symposium of Hybrid catalysts in innovative area, "Molecular transformation by supported alloy nanoparticle catalysts" 2018/1/30 Nagoya University.
3. 17th Lecture ship of hokkaido division of japan petroleum institute "Approach to realization of low-carbon society based on hydrogen energy" (invited lecture) 2018/1/26 Kitami institute of technology
4. Zasshikai seminar 1709th, 「Synthesis and characterization of nano-sized alloy catalyst (Invited lecture)」2017/12/19 （The University of Tokyo, 3F Lecture Room, Chemistry Main Bldg.）
5. 7th CSJ chemistry festa 2017, "Function of niobium and tantalum oxide as solid acid catalyst and photo catalyst" (invited lecture) 2017/10/19 Tower Hall Funabori
6. 120th CatSJ Meeting "Approach to realization of low-carbon society based on hydrogen energy", 2H10 (invited lecture) 2017/9/13 Ehime University
7. The 4th colloquium of Center for Functional Nano Oxide "Catalysis of niobium oxide; acid-base catalysis and photocatalysis" (invited lecture)」2017/5/26（Hiroshima Unicversity）
8. "Hydrosilylation of Unsaturated Organic Molecules over Supported PdAu Alloy Catalysts", H. Miura, K. Endo, R. Ogawa, S. Sasaki, T. Shishido, 16th Japan-Taiwan Joint Symposium on Catalysis January, 29-31, 2018 Kyoto, Japan

■Academic Meeting

＊International

1. Steam Reforming of Dimethyl Ether over Solid Acid Catalyst Coupled with Cu-based Catalyst, E. Kawai, Y. Kubo, H. Miura, T. Shishido, 16th Korea-Japan Symposium on Catalysis May 15-17, 2017 Hokkaido, Japan
2. Hydrogenolysis of glycerol to C3 diols over $Pt/WO_3/Al_2O_3$ and $Pd/L\text{-}Nb_2O_5$, T Aihara, H Kobayashi, S Feng, H Miura, T Shishido, 16th Korea-Japan Symposium on Catalysis (16KJSC, Sapporo) May 15-17, 2017, Hokkaido, Japan
3. Hydrosilylation of Alkynes and α,β-Unsaturated Ketones by Supported PdAu Catalysts, H. Miura, K. Endo, R. Ogawa, S. Sasaki, T. Shishido, EUROPACAT 2017 August, 26-30, 2017 Florence, Japan
4. Promotion effect of a tiny amount of platinum on the activity of Ni/TiO_2 catalyst for the selective hydrogenation, K. Noguchi, H. Miura, T. Shishido, EUROPACAT 2017 August, 26-30, 2017 Florence, Japan
5. Steam reforming of dimethyl ether over $Cu/ZnO/Al_2O_3$ coupled with H-ZSM-5: Effect of SiO_2/Al_2O_3 ratio on the activity, E. Kawai, H. Miura, T. Shishido, The 2nd International Symposium on Hydrogen Energy–based Society November 20-21, 2017 Tokyo, Japan
6. Selective catalytic reduction of NO with CO and C_3H_6 over $Rh/NbOPO_4$, S. Imai, H. Miura, T. Shishido, The 8th Japan-China Workshop on Environmental Catalysis December 5-6, 2017, Tsukuba, Japan
7. The effect of WO_3 loding on the activity of $Pt/WO_3/ZrO_2$ catalysts for hydrogenolysis of tetrahydrofurfuryl alcohol, Feng, Shixiang・Nagao, Aiko・Miura, Hiroki・Shishido, Tetsuya, 4th International Congress on Catalysis for Biorefineries ,11-15, December, 2017, Lyon, France

＊Domestic

See the annual report in Japanese (36 articles)

■Awards

1. Poster Award ''Development of supported Pd catalysts effective for hydrogen evolution from ammonia borane" Mitsuhiro Tominaga, Kengo Nakajima, Hiroki Miura, Tetsuya Shishido， 119th CatSJ Meeting (21-22 March 2017, Tokyo Metropolitan University).
2. Poster Award ''Dehydrogenative coupling of alcohols by Cu/ZrO_2" Karin Nakahara, Kengo Nakajima, Hiroki Miura, Tetsuya Shishido， 119th CatSJ Meeting (21-22 March 2017, Tokyo Metropolitan University).
3. Poster Award ''Study on selectivity control in hydrogenolysis of glycerol over supported metal catalysts" Takeshi Aihara, Hiroki Miura, Tetsuya Shishido， 119th CatSJ Meeting (21-22 March 2017, Tokyo Metropolitan University).
4. Poster Award ''Preparation of sulfo-functionalized siloxane gel catalysts with high hydrophobic surface and their catalysis for ester hydrolysis" Shutaro Kameyama, Hiroki Miura, Tetsuya Shishido， 15th Catalyst workshop in Takaoka, August 1, 2017, Takaoka.
5. Poster Award ''Dehydration of glycerol over WO_3/Al_2O_3 catalysts" Katsuya, Asazuma, Hiroki Miura, Tetsuya Shishido， 11th Shokubai Dojo in Kochi, September 25, 2017, Kochi.
6. Excellent Poster Award ''Selective hydrogenolysis of glycerol over $Pt/WO_3/Al_2O_3$ catalysts" Takeshi Aihara, Hiroki Miura, Tetsuya Shishido， 7th CSJ chemistry festa 2017, Funabori. 17-19 October 2017, Tower Hall Funabori
7. Excellent Poster Award ''Dehydrogenation of ammonia borane over supported AuPd alloy catalyst." Mitsuhiro Tominaga, Kengo Nakajima, Hiroki Miura, Tetsuya Shishido,

7th CSJ chemistry festa, Funabori. 17-19 October 2017, Tower Hall Funabori

8. Excellent Poster Award ‘‘Interconversion between ammonium bicarbonate and ammonium formate over supported Pd alloy catalyst” Kengo Nakajima, Hiroki Miura, Tetsuya Shishido, 37th annual meeting of Hydrogen Energy Systems Society of Japan, (4-5 December 2017, Funabori (Tokyo)

Applied Chemistry Colloquium

369th 2017/4/21
Kazuhiko Nakabayashi (Division of Developmental Genomics, National Research Institute for Child Health and Development)
"Epigenomics: History and Perspectives in Biology and Medicine"

370th 2017/5/8
Jorge Boczkowski (INSERM, Paris Est Créteil University, France)
"Effects of manufactured Nanoparticles on inflammation"

371st 2017/7/21
Hiroki Sakaguchi (Tottori University)
"Development of Silicon-based Negative Electrodes for Next Generation Lithium-ion Battery"

372nd 2017/12/8
Masaru Yoshitake (Fuel Cell Development Information Center)
"Current trends and future prospects toward hydrogen and fuel-cell utilized society"

373th 2017/12/15
Takao Aoyagi (Department of Materials and Applied Chemistry, Nihon University)
"Design and Synthesis of Smart Polymer for Biomaterials"

364th 2018/1/16
Dr. Kenichiro Koshika (National Traffic Safety and Environment Laboratory)
"Research for FCVs and EVs in National Traffic Safety and Environment Lab."

365th 2018/1/30
Prof. Dr. Zeev Gross（Schulich Faculty of Chemistry, Technion – Israel Institute of Technology）
"Energy Relevant Processes Catalyzed by Corrole Metal Complexes"

Annual Report 2017

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