Faculty of Environmental Sciences
Division of Applied Chemistry

Graduate School of Environmental Sciences
Department of Applied Chemistry

Annual Report 2017
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## Reports from Research Groups

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Master’s course -17
Bachelor 4 -8

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 gases, such as carbon dioxide (CO₂). 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 CO₂ permeability by using the composite membrane containing surface-modified pearl-necklace shaped silica nanoparticles. Furthermore, the mechanism for the improvement of CO₂ permeability in these composite membranes was analyzed by utilizing the 13C-NMR spectroscopy with 13CO₂ 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 (PBI NF) 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
Reports from Research Groups

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 antioxidative 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).](image)

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](image)

![Figure 9. Schematic drawing of NIPAm molecules adsorbed on clay.](image)

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


### Books


Invited Lectures


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 Zn2+ ions for up-regulation of gene expression, The 3rd International Forum on Applied Chemistry (September, 2017)


11. Hiroyoshi Kawakami, Chemistry saves the earth, The 1st Advanced Research Forum, Tokyo Metropolitan University (June 2017).


Academic Meeting


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)


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)


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), 1Pv079 (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)


24. Hiroto Mikami, Yuki 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, Japan, 1P083 (May, 2017 ) (in Japanese)

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

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


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 Funaburi), 2P213 (June 2017)

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


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

34. Hiroto Mikami, Yuki Kameyama, Manabu Tanaka, Hiroyoshi 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 Funaburi, Japan, 2P212 (June, 2017 ) (in Japanese)

35. Hiroto Mikami, Yuki Kudo, Manabu Tanaka, Hiroyoshi kawakami, 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 Funaburi, Japan (Tower Hall Funaburi), 2P214 (June 2017)
44. Ryosuke Shinohara, Riku Kubota, Shochihiro Asayama, Hiroyoshi Kawakami, Single chain lipoid-coated biodegradable polymer nanoparticles having co-delivery activity of drugs / plasmid DNA, the 17th IUPAC International Symposium on MacroMolecular Complexes (MMC-17) (Waseda University), P08(August 28-31, 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 nanointerface 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, Shochihiro 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, Hiroyoshi Kawakami, Design and secondary battery application of solid polymer electrolyte based on nanofiber framework, The 66th SPSP Symposium (Ehime University), September 2017


60. Riku KUBOTA, Hiroyoshi KAWAKAMI, Mechanism of oxygen reduction reaction of water-soluble supramolecular system composed of metalloporphyrin / metalloporphyrin / Cucurbit[10]uril, The 67th Conference of Japan Society of Coordination Chemistry(Hokkaido University),September 2017


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)


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, P07 (October, 2017)(in Japanese)


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)

Patents
1. P2017-63039, Polymer Electrolyte Membrane and Fuel Cell, Hiroyoshi Kawakami, Manabu Tanaka, Tsukasa Watanabe
3. P2017-216187, Blend Nanofiber and Their Composite Membrane, Hiroyoshi Kawakami, Manabu Tanaka, Risa Sakaguchi
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
Reports from Research Groups

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Master’s course -14
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 porous 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

(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 antireflection surface and surper hydrophobic surface.

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

For the preparation of uniform sized nanoparticles, we have introduced membrane emulsification 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

2. Takashi Yanagishita, Toshiaki Kondo, and Hideki Masuda
Preparation of Renewable Antireflection Moth-Eye Surfaces by Nanoimprinting Using Anodic Porous Alumina Molds

3. Takashi Yanagishita, Taito Inoue, Toshiaki Kondo, and Hideki Masuda
Preparation of Monodisperse LiCoO₂ Hollow Particles by Membrane Emulsification Using Anodic Porous Alumina

4. Takashi Yanagishita, Masahiko Imaizumi, Toshiaki Kondo, and Hideki Masuda
Formation of Porous Al Particles by Anisotropic Etching

5. Toshiaki Kondo, Hayato Miyazaki, Takashi Yanagishita, and Hideki Masuda
Anodic Porous Alumina with Square Holes Through Lattice Conversion of Naturally Occurring Ordered Structure
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

7. Nhat Truong Nguyen, Imgon Hwang, Toshiaki Kondo, Takashi Yanagishita, Hideki Masuda, and Patrik Schmuki
Optimizing TiO₂ Nanotube Morphology for Enhanced Photocatalytic H₂ Evolution Using Single-Walled and Highly Ordered TiO₂ Nanotubes Decorated with Dewetted Au Nanoparticles

8. Takashi Yanagishita, Atsushi Kato, and Hideki Masuda
Preparation of Ideally Ordered Through-Hole Anodic Porous Alumina Membranes by Two-Layer Anodization

9. Ryoei Takakura, Tomoya Oshikiri, Kosei Ueno, Xu Shi, Toshiaki Kondo, Hideki Masuda, and Hiroaki Misawa
Water Splitting Using a Three-Dimensional Plasmonic Photoanode with Titanium Dioxide Nano-Tunnels

Effect of steric hindrance on surface wettabiliy of fine silica powder modified by n- or t-butyl alcohol

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

■Invited Lectures
*International
1. Hideki Masuda, Toshiaki Kondo, and Takashi Yanagishita
Synthesis 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 Functional 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

5. Toshiaki Kondo, Takashi Yanagishita, Hideki Masuda
Ideally Ordered Nanohole Array Obtained by Anodizing Pretextured Metals

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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Doctor’s course -0  
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 structure 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.

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.

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.

**Papers with Peer Review**


**Account**


**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”.

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**Figure.** Structure of molecular gyrotop and birefringence change.

**Figure.** Clutch-decluch function in a novel molecular gear.

**Figure.** A phenyldisilane which exhibits CT fluorescence.

**Figure.** A phenyldisilane which exhibits CT fluorescence.
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, Kentaro Yamaguchi, 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)
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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 Cs₄SiW₁₂O₄₀ was essential to show high catalytic activity for CO oxidation. The Au/Cs₄SiW₁₂O₄₀ showed extremely 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/Cs₄SiW₁₂O₄₀.

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 NH₃-selective catalytic reduction (NH₃-SCR) under mild conditions are demanded in the NO removal technologies. The V₂O₅ catalyst that we developed

Figure 2. Dependence of NO conversion on reaction temperature in SCR of NO with NH₃ using V₂O₅ and 2-3 wt%V₂O₅/TiO₂.

Master’s course -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 V₂O₅ with high specific surface area has higher activity than conventional industrial catalysts (2-3wt% V₂O₅/TiO₂) in the low temperature range. These results are expected to greatly contribute to the efficient 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 sp² 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/ZrO₂ 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, CeO₂-ZrO₂, further improved the catalytic activity of gold to give vinyl benzoate up to 92%.

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 consumed in enzymatic reactions. Generally, stoichiometric amount 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 H₂. Small Au clusters (<2 nm) deposited on basic supports (Au/CeO₂ and Au/hydrotalcite (HT)) hydrogenated NAD⁺ under 1.0 MPa H₂ 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 H₂ 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.
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/MOx. Mice peritoneal primary macrophages were exposed to 1–100 µg/mL particles of Au/TiO2 and TiO2 for 48 h. Neither Au/TiO2 nor TiO2 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 TiO2 but was much less pronounced for Au/TiO2. To examine this effect of Au/TiO2 in detail, lipopolysaccharide (LPS)-induced pro-inflammatory response was measured (Fig. 6).

When TiO2 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/TiO2. This result suggests that Au/TiO2 attenuates LPS-induced inflammation. The similar effect was also observed on Au/ZrO2. Although the Au-mediated anti-inflammatory mechanism remains unclear at this stage, this study revealed that Au/TiO2 and Au/ZrO2 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).

Papers with Peer Review


**Books**


**Invited Lectures**


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.


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


*International (Poster)*


*Domestic (oral)*

See the annual report in Japanese (13 articles)

*Domestic (poster)*

See the annual report in Japanese (8 articles)

**Awards**


**Others**

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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 electrochemical performance of all solid state rechargeable batteries using oxide-based solid 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.](image1)

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.](image2)

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 Li4B7O12Cl. 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 Li4B4M3O12Cl (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 Mg2+-ion-conducting ceramic Mg0.5−x(Zr1−xNbx)2(PO4)3 (x = 0.15) using Mg electrodes in vacuum, and demonstrated the dc conduction of Mg2+ ions in this compound directly (Fig. 5).

![Fig. 4 Crystal structure of the newly discovered lithium-ion-conducting compound Li4B4M3O12Cl (M = Al, Ga) and photograph of a glass-ceramic sample of M = Al after contact with Li metal.](image3)
Fig. 5 Arrhenisus plot of ac conductivity of \( \text{Mg}_{0.5-x}(\text{Zr}_{x-1} \text{Nb})_{x} \text{PO}_4 \) (\( x = 0.15 \)) pellets measured with blocking Pt and non-blocking Mg electrodes (left) and dc polarization profile of the pellet measured with Mg electrodes at 350°C (right).

**Papers with Peer Review**


6. Jungo Wakasugi, Hirokazu Munakata, Kiyoshi Kanamura, Improvement of sintering of \( \text{Li}_{6.25} \text{Al}_{0.25} \text{La}_{3} \text{Zr}_{2} \text{O}_{12} \) by using pre-heat treatment, Solid State Ionics, 309, 9–14 (2017).


9. Naoto Tezuka, Yuta Okawa, Koichi Kajihara, Kiyoshi Kanamura, Synthesis and characterization of lithium-ion-conductive glassceramics of lithium chloroboracite \( \text{Li}_{1+x} \text{B}_{2} \text{O}_{2+x} \text{Cl} \) (\( x = 0–1 \)), J. Ceram. Soc. Jpn. 125, 348-352 (2017).

10. Koichi Kajihara, Hayato Nagano, Takaoki Tsujita, Hirokazu Munakata, Kiyoshi Kanamura, High-temperature conductivity measurements of magnetization-conducting solid oxide \( \text{Mg}_{0.5} \text{Zr}_{x} \text{Nb}_{x} \text{PO}_4 \) (\( x = 0.15 \)) using Mg metal electrode, J. Electrochem. Soc. 164, A2183-A2185 (2017).

11. Koichi Kajihara, Naoto Tezuka, Mao Shojo, Jungo Wakasugi, Hirokazu Munakata, Kiyoshi Kanamura, \( \text{Li}_6 \text{Ba}_2 \text{M}_{2} \text{O}_{2} \text{Cl} \) (\( M = \text{Al}, \text{Ga} \)): an electrochemically stable, lithium-ion-conducting cubic boracite with substituted boron sites, Bull. Chem. Soc. Jpn. 90, 1279-1286 (2017).


**Books**

See the annual report in Japanese (3 articles)

**Invited Lectures**

1. Kiyoshi Kanamura, Interface Control of All Solid State Battery with Li Metal Anode, LLZAl Electrolyte and LiMO₂ Cathode, PACRIM12, May, 2017, Waikoloa, Hawaii, USA


6. Kiyoshi KANAMURA, Kyoko KOZUKA, Takeshi KIMURA, Mao SHOJII, 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


10. Hirokazu Munakata, Jungo Wakasugi, Kyoko Kozuka, Takeshi Kimura, Mao Shoji, Kiyoshi Kanamura, Electrode Fabrication for All-solid-state Rechargeable Lithium Batteries using \( \text{Li}_{6.25} \text{Al}_{0.25} \text{La}_{3} \text{Zr}_{2} \text{O}_{12} \) Solid Electrolyte, ICACC2018, Jan., 2018, Daytona Beach, Fla. USA

**Academic Meeting**

**International**


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 Kamamura, 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 LiCoO₂ and Li₇La₃Zr₂O₁₂ 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
8. T. Mandai, K. Kanamura, A Key Concept of Utilization of Both Magnesium Chloride and Imide Salts for High Temperature Rechargeable Mg Battery Electrolytes, 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 Terukaz, Mao Shoji, Jungo Wakasugi, Hirokazu Munakata, Kiyoshi Kanamura, Li₄Ba₂M₆O₁₆Cl (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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Master’s course -15
Bachelor 4 -7

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

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

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.

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.
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 TiO2 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

■Books

+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.
5. Unique reaction field provided by two-dimensional materials in special session (Next-generation photofunctional materials innovated by dimensional reaction fields), S. Takagi, The 98th CSJ Annual Meeting.

■Academic Meeting
★International
Reports from Research Groups

**Domestic**
See the annual report in Japanese (20 articles)

**Patents**

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Master’s course -4
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 thiocyanate ion or 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 1H 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 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 Energy optimized structure of pyrazine-bridged Ru4 molecular square

2. Development of Novel Ionic Aggregation-Induced Emission (AIE) Fluorophores
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 photo-stability, 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 photo-stability, 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 derivatives. On the basis of the results above, a series of bridged tetraphenylpyridinium dimers were designed and prepared. The solid-state Φf 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.

Therefore, in this study, in order to elucidate the reactivity and the regioselectivity, the photoreaction of polycyclic pyridinium 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-tetraphenylypyridinium 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**


**Academic Meeting**

*International*


*Domestic*


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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 capillary gas chromatography and capillary electrophoresis. Currently, the technique is applied to on-line sample pre-concentration for capillary electrophoresis and to liquid-liquid extraction.

![Image](image1.png)

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 acceleration 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 reaction 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.

![Image](image2.png)
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 source and is not affected by background noise derived from the light source. 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 sensor 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 suburban 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 sulfurdioxide 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 gas sensor was demonstrated.

13. Atmospheric trace gas measurements using small gas sensor
Shungo KATO

Atmospheric trace gases was measured 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 chromatigraphy/Reduction gas detector system was constructed for low level hydrogen measurements. 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

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, Quishi 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

4. Hulie Zeng, Sifeng Mao, Yong Zhang, Hizuru Nakajima, Katsumi Uchiyama
Reversibly electro-controllable polymer brush for electro-switchable friction

5. Hulie Zeng, Yong Zhang, Hizuru Nakajima, Katsumi Uchiyama
Reversibly electro-switchable poly-allyloxy hydroxypropyl...
sulfonate branched brushes and its applications

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 gynoxyl at suburban site in Tokyo during summer season

Missing Ozone-Induced Potential Aerosol Formation at a Suburban Deciduous Forest
Atmospheric Environment, 2017, 171, pp.91-97

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 Katsumi, 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 International Convention & Exhibition Center, 6p-CA-K2

Academic Meeting

International
1. Katsumi Uchiyama
The use of an inkjet injection technique for quantitative online electrophoretically mediated micro-liquid chromatography
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, Kazuhiro Miura
CO and O3 observation at the summit of Mt. Fuji during summer
2017 Symposium on Atmospheric Chemistry and Physics at Mountain Sites, Gotemba

Ten years research at Mount Fuji research station
2017 Symposium on Atmospheric Chemistry and Physics at Mountain Sites, Gotemba

Aerosol chemistry in summer at the top of Mt. Fuji
2017 Symposium on Atmospheric Chemistry and Physics at Mountain Sites, Gotemba

6. Ryota Kataoka, Kazuhiro Miura, Masahiro Momoi, Yoko Iwamoto, Masanori Yabuki, Katsuhito 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

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

Observation of gaseous mercury at the top and the foot of Mt. Fuji
2017 Symposium on Atmospheric Chemistry and Physics at Mountain Sites, Gotemba

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, Kazuhiro 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

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 Katsumi, Katsumi Uchiyama
Effect of water activity on enzymes adsorbed on biomass charcoal in organic media
Third International Conference on Science, Engineering &
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 (27 articles)

■Awards
1. Moeko Osashima (Master's course 1 years)
   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
Reports from Research Groups

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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 (TiO₂) 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-pinacoloborylbenezoxyl 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 red-violet to blue. For practical applications, the related drop-cast paper strips were fabricated to visually detect hydrogen peroxide vapor.

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.

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[1,2,3]oxazaborinine-type dibenzo-BODIPYs was newly synthesized and incorporated into photoelectric devices. The resultant devices would be applicable to near-infrared absorbing photodetectors.

Papers with Peer Review

Invited Lectures

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

Academic Meeting

International

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
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
6. Synthesis of a quinoline amide dye with a boronic acid-grafting group and its application to chemosensors, Uji; Pramoto, Yuji Kubo, IF5-36, 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, 3H1-07, The 98th CSJ Annual meeting Nihon University, 2018, Mar 22nd

8. Dynamics of water reduction by dye-sensitized photoelectrochemical cells incorporating 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 conversion 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 NOx (NO and NO2) into N2 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 C3H6 under various simulated exhausts with different air-to-fuel ratios. As a result, Rh/NbOPo4 showed higher catalytic activity than conventional Rh/Al2O3 catalyst. Especially, Rh/NbOPo4 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 medicines 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 catalysts 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

2. Dynamic Behavior of Rh Species of Rh/Al2O3 Model Catalyst During Three-Way Catalytic Reaction – An Operando XAS Study


4. Coconcerted Functions of Surface Acid-Base Pairs and Supported Copper Catalysts for Dehydrogenative Synthesis of Esters from Primary Alcohols


**Invited Lectures**


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) J 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 Funaburi

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) J 2017/5/26 (Hiroshima University)

**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/$\text{WO}_3/\text{Al}_2\text{O}_3$ and Pd/L$\text{Nb}_2\text{O}_5$, T Aihara, H Kobayashi, S Feng, H Miura, T Shishido, 16th Korea-Japan Symposium on Catalysis (16KJSC, Sapporo) May 15-17, 2017, Hokkaido, Japan


6. Selective catalytic reduction of NO with CO and $\text{C}_3\text{H}_8$ over Rh/Nb$\text{PO}_4$, S. Imai, H. Miura, T. Shishido, The 8th Japan-China Workshop on Environmental Catalysis December 5-6, 2017, Tsukuba, Japan


**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).


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).


6. Excellent Poster Award “Selective hydrogenolysis of glycerol over Pt/$\text{WO}_3/\text{Al}_2\text{O}_3$ catalysts” Takeshi Aihara, Hiroki Miura, Tetsuya Shishido, 7th CSJ chemistry festa 2017, Funaburi. 17-19 October 2017, Tower Hall Funaburi

7. Excellent Poster Award “Dehydrogenation of ammonia borane over supported AuPd alloy catalyst.” Mitsuhiro Tominaga, Kengo Nakajima, Hiroki Miura, Tetsuya Shishido,
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”