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Reports from Research Groups

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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 (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, especially pearl-necklace shaped silica nanoparticles that have originally inter-connected structures (Figure 1). By using these nanoparticles, we have succeeded in fabricating novel polymer composite membranes with excellent CO₂ permeability ranked at the highest level in the world. Furthermore, the mechanism for the improvement of CO₂ permeability in these composite membranes was analyzed by utilizing the 129Xe-NMR spectroscopy and gas adsorption measurements.

Figure 1. Schematic illustration of the polymer composite membranes containing the surface-modified silica nanoparticles with pearl-necklace 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 tried to improve their performances via the acid/base layer-by-layer surface modification process of the nanofibers to increase the effective conductive pathways at the interface of the nanofibers and the matrix polymer (Figure 2). The novel nanofiber composite membrane showed ca. ten times higher proton conductivity than the conventional composite membranes under low humidity conditions, which are assumed as future fuel cell operation conditions.

Figure 2. Schematic illustration of the polymer electrolyte composite membranes based on the layer-by-layer surface-modified nanofibers.

3. Study of Electrospun Nanofibers
Hiroyoshi KAWAKAMI, Manabu TANAKA

Doctor’s course -1
Master’s course -15
Bachelor 4 -9
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. It was revealed that the improvement of the conductivity was derived not only from the intrinsic high ion conductivity of the nanofibers themselves but also from the suppression of crystallization of the matrix polymer at low temperatures. Then, lithium ion batteries using the nanofiber composite membranes were prepared and evaluated to demonstrate successful fabrication of all-solid-state secondary batteries.

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 investigated catalytic activity of supramolecular bimetallic complex composed of metallo porphyrin, metallo bis(bipyridine) and cucurbit [10] uril (CB[10]). The complex can be prepared from variety of metallo porphyrin and metallo bis(bipyridine). Furthermore, the supramolecular bimetallic complex exhibited catalytic reduction of carbon dioxide (CO2) and oxidation of water (H2O).

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 epigenetics control carrier (EpC) carrier for novel therapy for diabete. The EpC carrier enhanced the number of insulin-secreting cells. Besides, we have synthesized novel block polymer targeting histone for artificial control of chromatin structure. The block polymer provided the potential 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 SOD Mimic
Hiroyoshi KAWAKAMI, Shoichiro ASAYAMA, Riku KUBOTA

Superoxide dismutase (SOD) is well known to efficiently dismute superoxide radicals as most important antioxidant. We demonstrated that a water-soluble cationic Mn-prophyrin with SOD 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 (MndMImP3P). The resulting nanoparticle exhibited remarkable antioxidative activity. The mechanistic study of the antioxidative activity suggested that Mn-porphyrin was accumulated in mitochondria and suppressed reduction of mitochondrial membrane potential.

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\textsuperscript{2+} are expected to satisfy unmet medical needs (Figure 7).

In this year, by use of our cholesterol end-modified poly(ethylene glycol) (Chol-PEG), we have established novel noncovalent PEylation methods for liquid-phase (DDS) and solid-phase (Biocompatible materials) biomaterials. As DDS, we have succeeded in the insulin PEylation for in vivo diabetes therapy. As biocompatible materials, we have succeeded in the surface PEylation of poly(propylene). Furthermore, we are focusing on the mono-ion complex and Zn\textsuperscript{2+} delivery.

![Image](https://via.placeholder.com/150)

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. The following was examined in this year. The mixed clay hybrid gel was developed. POM observation revealed anisotropy of the hybrid gel prepared in a magnetic field. Anisotropy of the hybrid gel was increased by adding other clay which was hardly aligned by a magnetic field, resulting in improvement of mechanical properties of the gel.

![Image](https://via.placeholder.com/150)

Figure 8. POM images of organic/inorganic hybrid gel prepared in a magnetic field of 3 T (a) and stress-strain curves of the gel (b).

### Papers with Peer Review

### Reviews

### Books
2. Masafumi Yamato, Improvement of thermal properties on heat radiation and high heat-resistant materials and technology for heat measure, Technical information institute, p.p. 66-71

Invited Lectures

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

Academic Meeting

5. Yutaro Asaba, Risa Shimazaki, Kazuhiro Nakabayashi, Shoichiro Asayama, and Hiroyoshi Kawakami, Control of Epigenetics Modification by Lipid-Coated Biodegradable Nanoparticles for the Novel Cancer Therapy, 10th World Biomaterials Congress, Final Program, p. 221, P.2148 (May, 2016).

18. Riku Kubota, Manabu Tanaka, Hiroyoshi Kawakami, Preparation of proton conductive blend nanofiber composite membranes and characterization of their fuel cell properties, The Annual Meeting of the Society of Fiber Science and Technology, Japan, (Tower Hall Funabori), (June 2016) (in Japanese)


21. Eizo Ushijima, Yuji Iwata, Masafumi Yamato, Patternning of nanoparticles using a magnetic modulator, 7th International Workshop on Materials Analysis and Processing in Magnetic Field, June 2016, (Providence, USA) (June 2016)


27. Shochiro Asayama, Mizuki Sakata, Hiroyoshi Kawakami, See the annual report in Japanese (July 2016)


32. Masafumi Yamato, Shoma Machizuki, Noriyuki Hirot, and Hiroyoshi Kawakami, Birefringence of clay mixed nano composite gel polymerized in a magnetic field, 65th Symposium of Macromolecules, University of Kanagawa, (1T17) (September, 2016) (in Japanese)


35. Tsukasa Watanabe, Manabu Tanaka, and Hiroyoshi Kawakami, Preparation and evaluation of ion conductive polymer nanofiber framework for all-solid-state lithium ion battery, 65th Symposium on Macromolecules, Japan, Vol. 65, No. 2, p. 39 (1X18) (September 2016) (in Japanese)


37. Takushi Shimane, Tsukasa Watanabe, Manabu Tanaka, Hiroyoshi Kawakami, Preparation of nanofiber framework composite electrolyte membranes based on lithium ion conductive polymer nanofibers for future secondary battery applications, The 65th Symposium of Macromolecules, 3Pa049 (September, 2016) (in Japanese)

38. Takahito Makinouchi, Manabu Tanaka, Hiroyoshi Kawakami, Fabrication and characterizations of surface-modified nanofiber framework composite membranes for proton conductivity enhancement, The 65th Symposium on Macromolecules, Kanagawa University, 3Pb052 (September, 2016) (in Japanese)


42. Risa Sakaguchi, Manabu Tanaka, Hiroyoshi Kawakami, Preparation of acid/base blend polymer nanofibers and their fuel cell application, 65th Symposium on Macromolecules, (Kanagawa University), (Sep. 2016) (in Japanese)

43. Shochiro Asayama, Mizuki Sakata, Hiroyoshi Kawakami, See the annual report in Japanese (September 2016)

44. Ryusuke Shinohara, Shochiro Asayama and Hiroyoshi Kawakami, Epigenetics control by biodegradable nanoparticles coated with alkyl amine, 64th Symposium on Macromolecules, 2Pc109 (September, 2016) (in Japanese)


49. Emika Narazaki, Shiochiro Asayama, Hiroyoshi Kawakami, See the annual report in Japanese (September 2016)

50. Yuta Inafune, Tsukasa Watanabe, Manabu Tanaka, Hiroyoshi Kawakami, Preparation of polymer electrolyte composite membranes based on lithium ion conductive nanofibers, The 65th Symposium on Macromolecules, Kanagawa University, 3Pb048 (Sep.2016) (in Japanese)


55. Hiroto Mikami, Yuri Kameyama, Manabu Tanaka, Hiroyoshi Kawakami, CO2 permeability evaluation of polyimide composite membranes containing mixed silica nanoparticles with different morphologies. 65th symposium of Macromolecules, Kanagawa University, Japan, 2Pb074 (September, 2016) (in Japanese)

56. Hideaki TANIGUCHI, Taiga TAKABE, Riku KUBOTA, Hiroyoshi KAWAKAMI, Synthesis and catalytic application of a novel water-soluble supramolecule composed of Fe-porphyrin/Fe(bpy)2/Cucurbit[10], The 66th Conference of Japan Society of Coordination Chemistry (Fukuoka University), 1PF-03, (September, 2016) (in Japanese)


60. Takushi Shimane, Yuta Inafune, Tsukasa Watanabe, Manabu Tanaka, Hiroyoshi Kawakami, Preparation of nanofiber framework composite electrolyte membranes based on lithium ion conductive solid polymer nanofibers for future secondary battery application, The 57th Battery Symposium, 1G05, Makuhari Messe (November, 2016) (in Japanese)


63. Shiochiro Asayama, Mizuki Sakata, Hiroyoshi Kawakami, See the annual report in Japanese (November 2016)


65. Yuta Inafune, Tsukasa Watanabe, Manabu Tanaka, Hiroyoshi Kawakami, Fabrication of solid electrolyte based on lithium ion conductive nanofiber framework for bipolar stacked battery application, The 85th Musashino area polymer association, Kougakuin University, P02 (Nov.2016) (in Japanese)

66. Takahiro Ogura, Takeru Wakiya, Manabu Tanaka, and Hiroyoshi Kawakami, Preparation of composite thin membranes consisted of acid-doped nanofiber frame works and their influence to fuel cell electrolyte membrane, 85th Musashino area polymer forum, Kogakuin University, Japan, P05 (November, 2016) (in Japanese)

67. Shun Nakazawa, Kazunori Hara, Tsukasa Watanabe, Manabu Tanaka, and Hiroyoshi Kawakami, Preparation of lithium single-ion-conducting nanofiber composite electrolyte membranes and their application to secondary batteries, 85th Musashino area polymer association, Kogakuin University, Japan, (P12) (Nov. 2016) (in Japanese)

68. Hiroto Mikami, Yuri Kameyama, Manabu Tanaka, Hiroyoshi Kawakami, Gas permeability evaluation of polyimide composite membranes containing mixed silica nanoparticles with different morphologies. 65th symposium of Macromolecules, Kanagawa University, Japan, P16 (November, 2016) (in Japanese)


71. Yuki Kudo, Manabu Tanaka, Masafumi Yamato, Hiroyoshi Kawakami, CO2 permeability evaluation and analysis of PIM-1 composite membranes containing surface-modified silica nanoparticles, 54th Symposium on Polymer and Water, Japan, p. 10 (December, 2016) (in Japanese)

72. Takahito Makinouchi, Manabu Tanaka, Hiroyoshi Kawakami, Fabrication and characterizations of surface-modified nanofiber framework composite membranes for fuel cell operation at low humidity, The 54th Symposium
on Polymer and Water Japan, P13, Tokyo Institute of Technology (December, 2016) (in Japanese)
73. Shoichiro Asayama, Mizuki Sakata, Hiroyoshi Kawakami, See the annual report in Japanese (March 2017)

■ Patents
2. P2016-102287A, Nanofiber, nanofiber assembly, composite membrane, solid polymer electrolyte, and lithium ion battery, Hiroyoshi Kawakami, Manabu Tanaka, Tsukasa Watanabe
6. P2016-110367, Composite nanofiber and electrolyte membrane, Hiroyoshi Kawakami, Manabu Tanaka, Risa Sakaguchi
7. P2016-163160, Multielectron redox catalyst, Hiroyoshi Kawakami, Riku Kubota, Hideaki Taniguchi, Taiga Takabe
8. P2016-162455, Surface-modified nanofiber, electrolyte membrane, fabrication process of electrolyte membrane, membrane electrode assembly, and polymer electrolyte fuel cell, Hiroyoshi Kawakami, Manabu Tanaka, Takahito Makinouchi
9. P2016-163081, Gas separation membrane containing variant silica nanoparticles, Hiroyoshi Kawakami, Manabu Tanaka, Yuri Kameyama, Yuki Kudo, Hiroto Mikami, Tadayuki Isaji, Kazutoshi Kodata, Takamasa Kikuchi
10. P2016-211648, Polymer electrolyte membrane and fuel cell, Hiroyoshi Kawakami, Manabu Tanaka, Tsukasa Watanabe
11. P2016-162456, Fabrication process of electrolyte membrane and battery materials, Hiroyoshi Kawakami, Manabu Tanaka, Tsukasa Watanabe

■ Awards
1. Shoichiro Asayama, the Tokyo U-club, See the annual report in Japanese (May 2016)
2. Yuri Kameyama, Gas permeation property evaluation of polyimide composite membranes containing novel surface-modified nanoparticles, The student poster award, 38th Annual Meeting on The Membrane Society of Japan, Waseda University (May 2016)
4. Yuki Kudo, Analysis of the CO2 permeation mechanism of composite membranes containing surface-modified silica nanoparticles, The excellent poster award, 65th Symposium on Macromolecules, Kanagawa University (September 2016)
5. Takahito Makinouchi, Fabrication and characterizations of surface-modified nanofiber framework composite membranes for proton conductivity enhancement, The excellent poster award, 65th Symposium on Macromolecules, Kanagawa University (September 2016)
6. Yuma Yokokawa, synthesis and evaluation of β-CD-modified anionic polymer for inhibition and degradation of amyloid β aggregation, The excellent poster award, 65th Symposium on Macromolecules, Kanagawa University (September 2016)
7. Yuki Kudo, CO2 permeability evaluation and analysis of PIM-1 composite membranes containing surface-modified silica nanoparticles, The excellent student presentation award, 54th Symposium on the Interaction between Polymer and Water and Separation Science, Tokyo Institute of Technology (December 2016)
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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 nanoflere 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

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 antirefrefection 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,
   Formation of porous Al particles by anisotropic anodic etching

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

3. Ryoohe Takakura, Tomoya Oshikiri, Kosei Ueno, Toshiaki Kondo, Hideki Masuda, and Hiroaki Misawa
   Water Splitting Using a Three-dimensional Plasmonic Photoanode with Titanium Dioxide Nano-tunnels
   Green Chem., in press.

4. Takashi Yanagishita and Hideki Masuda
   Facile Preparation of Porous Alumina Through-Hole Masks for Sputtering by Two-Layer Anodization

5. Toshiaki Kondo, Shota Hirano, Takashi Yanagishita, Nhat Truong Nguyen, Patric Schmuki, and Hideki Masuda


Reviews and Books
See the annual report in Japanese (6 articles)

Invited Lectures
International
1. Hideki Masuda, Toshiaki Kondo, Takashi Nakazono, and Takashi Yanagishita Growth of Ordered ZnO Nanorods Arrays Using Anodic Porous Alumina Templates 229th ECS Meeting, 2016/5, San Diego

2. Toshiaki Kondo, and Hideki Masuda Formation of Metal Nanostructure Array and Its Application to Plasmonic Devices International Workshop on Nanostructure-Based Chemistry and Light-Energy Conversion, 2016/6, Tokyo


6. Hideki Masuda, Takashi Yanagishita, and Toshiaki Kondo Fabrication of Highly Ordered Anodic Porous Alumina and Its Applications to Functional Nanodevices PRiME 2016/230th ECS Meeting, 201/10, Hawaii


Domestic
See the annual report in Japanese (9 articles)

Academic Meeting
International
1. Toshiaki Kondo, Takashi Yanagishita, Hideki Masuda, Three-dimensional waveguide obtained using anodic porous alumina 2016 MRS Fall Meeting, 2016/11, Boston

Domestic
See the annual report in Japanese (39 articles)

Patents
See the annual report in Japanese (4 articles)

Awards
See the annual report in Japanese (2articles)
Developments 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 Gyropot

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 gyropot 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-triprycyl)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-triprycyl)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


Invited Lectures

1. Yusuke Inagaki, Molecular arrangements and synamics in a Crystalline State, The first workshop for young organic chemist, 2016.11.9-10, Kyoto University


International

1. Wataku Setaka
Dielectric Properties of Crystalline Molecular Gyropots with a Dipolar Rotor
The 2nd International Symposium on Stimuli-responsive Chemical Species for the Creation of Functional Molecules,
2. Watasu Setaka
Phenylene-Bridged Macrocage Compounds as Molecular Gyrotops in Crystalline State
The 2016 Asian Crystallographic Association Conference (AsCA), 2016.12.3-8., Hanoi University of Science and Technology, Hanoi, Vietnam (MS11.O03)

3. Miyako Tsurunaga, Yusuke Inagaki, Watasu Setaka
A Novel Thiophene-Dioxide Bridged Molecular Gyrotop as a Candidate for Dielectric Material

4. Kohei Sato, Yusuke Inagaki, Watasu Setaka
p-Benzquinone-Bridged Macrocages as Potential Electron Carriers

5. Watasu Setaka
Synthesis and Structure of a Selenophene-bridged Macrocage as a Molecular Gyrotop
The 13th International Conference on the Chemistry of Selenium and Tellurium (ICCST-13), 2016.5.23-27, Nagaragawa Convention Center, Gifu, Japan

★ Domestic
See the annual report in Japanese (10 articles)

■ Awards
1. Miyako Tsurunaga received the excellent poster award at 6th CSJ Chemistry Festa, the Chemical Society of Japan (14-16 October 2016, Funabori (Tokyo)). The title of her presentation was “Synthesis of Novel Thiophene-dioxide Bridged Molecular Gyrotops and their Dynamic Properties in Crystalline State”.

2. Mr. Kazuma Okamura received Excellent Oral Presentation Award and Chemistry Letters Young Award at the 43rd Symposium on Main Group Element Chemistry (Dec. 8-10, 2016, Sendai Citizen Hall, Sendai). The title of his talk was “Synthesis and dynamics of germanium-linked molecular gears and their 5-coordinated derivatives”.
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Master’s course -1
Research student-1

Outlines of the Research

1. Gas Phase Reactions by Metal Oxide-Supported Gold Catalysts
Toru MURAYAMA, Takuya YOSHIDA, Takashi FUJITA, Dien Xuan LUONG, Masatake HARUTA

Gold nanoparticles were deposited onto niobium oxide (NbOx) prepared by hydrothermal method. We examined several kind of preparation methods and found that sol immobilization (SI) was suitable to deposit Au nanoparticles with a mean diameter of 3 nm. SI was superior to deposition-precipitation (DP), deposition-reduction (DR), and solid grinding (SG) in terms of minimizing the size of Au particles. Au/NbOx (SI) exhibited high catalytic activity (Fig. 1) and recorded 91% conversion at 28 °C.

![Fig.1 Relationships between gold particle size of Au/NbOx and turnover frequency (TOF) for CO oxidation at 20 °C.](image)

A size dependency of Au/Cs4SiW12O40 prepared by SI on CO oxidation was examined. The catalytic activity significantly decreased with an increase in the size of Au particles. The result suggested that a deposition of Au clusters smaller than 2 nm onto Cs4SiW12O40 is essential to show high catalytic activity (Fig. 2).

![Fig. 2 Catalytic activity for CO oxidation on Au/Cs4SiW12O40.](image)

Oxygen vacancy at Au–metal oxide interface plays an important role for CO oxidation at low temperature. To clarify the effect of the interaction between Au and metal oxides regarding to the formation of oxygen vacancy, catalytic activity of Au/ZnO was examined by verifying the calcination atmosphere. Au/ZnO calcined in H2 followed by O2 calcination (H2-573K) exhibited remarkably higher catalytic activity than that calcined in O2 (O2-523K). We also found that the reaction mechanism of Au/ZnO (H2-573K) for CO oxidation changed at
lower than \(-20\) °C. According to the oxygen temperature programmed desorption (O2-TPD) profiles (Fig. 3), a desorption peak at low temperature (353 K) was observed in Au/ZnO (H2-573K). This result implies that the calcination atmosphere affects the formation of oxygen vacancy at Au–oxide interface; calcination in H2 and then O2 might form active oxygen species that works at low temperatures.

2. Liquid Phase Reactions by Supported Metal Nanoparticle Catalysts
Tamao ISHIDA, Ayako TAKETOSHI, Masatake HARUTA

Ullmann coupling of iodobenzene catalyzed by supported Au NPs was studied using various kinds of metal oxide supports. Metal oxides having redox properties themselves, such as CeO2, Co3O4, MnO2, showed lower or poor catalytic activity than other supports. Conversion increased with the acidity of metal oxides, but selectivity decreased due to the formation of benzene as a by-product. As a result, amphoteric oxides, such as Al2O3, gave the highest biphenyl yields (Fig. 4). We also examined the size dependency and found that suitable Au particle size depend on the kinds of supports; smaller Au particles showed higher activity for Au/ZnO, but larger ones were better for Au/SiO2.

![Fig. 4](image_url) Relationship between electronegativity of supports and biphenyl yield for Ullman coupling.

Aliphatic ethyl esters are an important class of fine chemicals in application to fragrance and flavors. Oxidative esterification of aldehyde to ethyl ester was examined using octanal as a model compound (Scheme 1). The largest ester was obtained in high yield when Au was deposited as clusters smaller than 2 nm onto ZnO, Al2O3, Co3O4. We found that these catalysts worked efficiently under high concentrations in the aim of industrial applications.

![Scheme 1](image_url) Synthesis of ethyl octanoate from octanal.

3. Preparation of Supported Gold Clusters
Ayako TAKETOSHI, Dien Xuan LUONG, Tamao ISHIDA, Masatake HARUTA

We have studied a development of catalyst preparation methods using microwave (MW). Drying methods, oven, freeze-drying (FD), and MW, were compared by means of chemical state of Au after drying and the size of Au particles using X-ray absorption spectrometry. In case of Au/Al2O3, Au(III) completely remained after FD and MW drying. In contrast, ca. 50% of Au(III) was reduced to Au(0) after oven drying. After the reduction with H2, Au(III) was completely reduced in all cases. The size of Au particles were estimated by curve-fitting analyses to be 2.3, 1.9, and 1.6 nm for oven, FD, and MW drying, respectively. These values were in a good agreement with the high-angle annular dark field transmission electron microscopy (HAADF-STEM) observation. As a result, MW drying was superior method to produce the smallest Au clusters.

Solid grinding (SG) method is a useful preparation for inert supports to deposit Au clusters and simple, because Au can be deposited by just grinding the Au precursor, Me2Au(acac), and supports at room temperature under air followed by calcination. However, Me2Au(acac) is expensive and hardly obtained. Therefore, alternative Au precursors, which can be applied to SG, was studied. As a result, Au(TPy)(TFA)2, Au(TPy)boryxing, IPrAuOH, Au-thiomalic acid complex were found to be potential precursors (Fig. 5). In contrast, Au was aggregated when Au(TPy)Cl2 was used, suggesting that the presence of halogen as a ligand accelerated the aggregation of Au.

![Fig. 5](image_url) Scope of organogold complexes for solid grinding.

4. Synergistic Effects of Gold Nanoparticle Catalysts with Biofunctional Materials
Jun-ichi NISHIGAKI, Takashi FUJITA, Masatake HARUTA

We developed the catalytic reaction having synergistic/complementary effects by putting biological enzyme catalyst and artificial Au NPs catalyst together. NADH and NAD+ work as coenzymes that are consumed to reduce/oxidize substrates. Au NPs (1.4–4.2 nm) deposited on nanodiamond and metal oxides can oxidize NADH to NAD+ using O2 as an oxidant. Addition of these Au catalysts to dehydrogenase enzymeic oxidation reaction allows reproducing NAD+ from spent NADH to proceed enzymatic oxidation. This system requires only O2 as an additional reactant, which gives the potential for developing resource conservation and low environmental damage catalytic systems (Scheme 2). Optimization of reaction conditions is ongoing to improve yields.

![Scheme 2](image_url) Catalytic transformation of NADH to NAD+ by using gold catalysts.

As an additional result, Au clusters deposited on basic metal oxides, such as hydrotalcite and CeO2, catalyzed the reduction of NAD+ to NADH with H2 (1 MPa) at low temperature (37°C), suggesting that the Au catalysts can also be used as a coenzyme reproducing system in a dehydrogenase reduction process (Scheme 3).

![Scheme 3](image_url) Hydrogenation of NAD+ to NADH by using gold catalysts for glucose oxidation with GDH.

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For the full version of the document, please refer to the original source.
For application of supported Au nanoparticles (NPs) into nanomedicine, cytotoxicity of several kinds of supported Au NPs for HeLa cells (human cell line derived from cervical cancer cells). Although SiO2 did not show cytotoxicity, the deposition of Au onto SiO2 improved the cytotoxicity. On the other hand, no difference was observed for TiO2 with or without Au NPs. The deposition of Au NPs affected the cytotoxicity depending on the metal oxide supports. Relationships between cytotoxicity and acid-base properties of support surface will be discussed in the near future.

Papers with Peer Review


Reviews


See the annual report in Japanese (4 articles)

Books


Invited Lectures

Reports from Research Groups

Catalyzed by Gold Nanoparticles”, Dalian Institute of Chemical Physics, China, 2017.3.13

See the annual report in Japanese (2 lectures)

**Academic Meeting**

**International (oral)**


2. T. Fujita, "CO oxidation on metal oxide-supported gold catalysts: Correlation between the catalytic activity and metal-oxygen binding energy of supports", TMU-Yantai Univ. Joint Workshop, Tokyo Metropolitan University (TMU), 2016.10.5


**International (poster)**


2. T. Murayama, M. Haruta, "Deposition of gold nanoparticles on "solid acid" metal oxide", The 16th International Congress on Catalysis (ICC-16), Beijing, China, 2016.7.5


5. M. Mino, T. Murayama, M. Haruta, “NH3-SCR of NO on Vanadium Oxides at Low Temperature”, International Conference on Catalysis and Chemical Engineering, Baltimore, USA, 2017.2.23

**Domestic (oral)**

See the annual report in Japanese (11 articles)

**Domestic (poster)**

See the annual report in Japanese (14 articles)

**Patents**


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Doctor’s course -8
Master’s course -17
Bachelor 4 -8

Outlines of the Research

1. Research on Rechargeable batteries

Kiyoshi KANAMURA, Hirokazu MUNAKATA

The development of new rechargeable batteries with high energy density and excellent safety was promoted in order to realize a sustainable society based on the effective use of energy, in which we particularly investigated the use of lithium metal with ~10 times higher capacity than that of currently-used graphite as an anode material. In addition, we investigated the use of solid electrolytes instead of conventional liquid ones to explore new battery designs (Fig. 1).

Fig. 1 Photograph of all-solid-state battery developed by using a solid electrolyte.

The fundamental research on rechargeable magnesium batteries was also promoted, in which the electrolyte system appropriate for reversible dis/solution/deposition of magnesium metal was particularly investigated (Fig. 2).

Fig. 2 Dissolution/deposition behavior of magnesium in various electrolyte systems.

2. Research on Fuel cells

Kiyoshi KANAMURA, Hirokazu MUNAKATA

Toward the realization of a hydrogen society, the development of a new fuel cell system that works at intermediate temperatures of ~150 °C under non-humidified conditions was promoted. A prototype fuel cell was developed based on a new electrolyte system with ionic liquids, and its operation was succeeded at 160 °C without humidification (Fig. 3).

Fig. 3 I-V and I-W curves of the developed prototype fuel cell at 160 °C 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. Environmentally-friendly synthetic routes to prepare polysilsesquioxane (PSQ) liquids without using cosolvent (e.g. alcohols and other organic solvents) were developed. This financial year we found that the liquid-liquid phase separation is not essential for the preparation of PSQ liquids (Fig. 4). We also examined photochemical reactions and photoluminescence of interstitial Cl2 molecules and related interstitial chlorine species in synthetic silica glasses, which are important for optical materials of photolithography, and identified a new interstitial molecule ClClO (Fig. 5).

Fig. 4 Synthesis of polysilsesquioxane liquids.

Galvanostatic plating/stripping

Symmetric cell

Fig. 5 Aged solution

Mixing & Aging

Drying

PSQ liquid

RS(OMe)3

HNO3 aq.

RS(OTf)3

R = Et, n-Pr, n-Bu

Similar structure & instability

Galvanostatic plating/stripping

Symmetric cell

Fig. 1 Photograph of all-solid-state battery developed by using a solid electrolyte.
Fig. 5 Reactions of interstitial chlorine-related species in synthetic silica glass.

Papers with Peer Review

1. Wenchao Yan, Jicheng Jiang, Wei Liu, Deye Sun, Erqing Zhao, Yongcheng Jin, Kiyoshi Kanamura, Effect of precipitators on the morphologies and electrochemical properties of Li$_{1.2}$Mn$_{0.54}$Ni$_{0.13}$Co$_{0.13}$O$_2$ via rapid nucleation and postsolvothermal method, Electrochimica Acta, 224, 2017, pp 161-170.


4. Jungo WAKASUGI, Hirokazu MUNAKATA, Kiyoshi KANAMURA, Thermal Stability of Various Cathode Materials against Li$_{1.25}$Al$_{0.25}$La$_{2}$Zr$_2$O$_7$ Electrolyte, Electrochemistry, 85, 2017, pp. 77-81.


8. Erqing Zhao, Furui Ma, Yongcheng Jin, Kiyoshi Kanamura, Pechini synthesis of high ionic conductivity Li$_{1.3}$Al$_0.3$Ti$_1.7$(PO$_4$)$_3$ solid electrolytes: The effect of dispersant, Journal of Alloys and Compounds, 680, 2016, pp. 646-653.

9. Wenchao Yan, Jicheng Jiang, Wei Liu, Xiao Yan, Deye Sun, Yongcheng Jin, Jing Wang, Lan Xiang, Hirokazu Munakata, Kiyoshi Kanamura, Synthesis and Evaluation of Microsphrical Li$_{1.2}$Mn$_{0.54}$Ni$_{0.13}$Co$_{0.13}$O$_2$ through Carbon Dioxides-assisted Co-precipitation Method for Lithium-ion Battery, Electrochimica Acta, 212, 2016, pp. 16-24.


13. Mao Shoji, Hirokazu Munakata and Kiyoshi Kanamura, Fabrication of All-Solid-State Lithium-Ion Cells Using Three-Dimensionally Structured Solid Electrolyte Li$_{1.25}$Al$_{0.25}$La$_{2}$Zr$_2$O$_7$ Pellets, Frontiers in Energy Research, 4, 2016, article 32.

Reports from Research Groups


**Reviews**
See the annual report in Japanese (6 articles)

**Books**
See the annual report in Japanese (2 articles)

**Invited Lectures**
See the annual report in Japanese (12 articles)

**Academic Meeting**


2. Mao Shoji, Takashi Narushima, Takeshi Kimura, Hirokazu Munakata, Kiyoshi Kanamura, Investigation of Li source influence on the sinterability of garnet-type solid electrolyte Li₄.25Al₂.25La₂Zr₂O₁₂, 229th ECS MEETING, May 2016, Sandiego, USA.

3. Takeshi KIMURA, Kyoko KOZUKA, Naoto SAITO, Mao SHOJI, Takashi NARUSHIMA, Hirokazu MUNAKATA, Kiyoshi KANAMURA, Formation of LiCoO₂ / Li₂BO₃ Composite Cathode on Al doped Li₂La₂Zr₂O₁₂ Solid-State electrolyte by Aerosol Deposition Method, 229th ECS MEETING, May 2016, Sandiego, USA.

4. L. Skuja, K. Kajihara, K. Smits, H. Hosono, Interstitial Chlorine Molecules in SiO₂ Glass, 11th International Symposium on SiO₂, Advanced Dielectrics and Related Devices, June 2016, Nice, France


6. H. Yamashita, T. Ogami, K. Kanamura, Effects of the carbon sources on the electrochemical properties of LiMn₀.₅Fe₀.₅PO₄/C for lithium-ion batteries, The 9th International Symposium on Inorganic Phosphate Materials (ISIPM-9), September 2016, Tokyo, Japan


16. T. Omura, Y. Yamada, Y. Noda, S. Miyamoto, H. Munakata,


19. Kiyoshi Kanamura, Development of Next Generation Batteries with Li Metal Anode, IMSE2016, October 2016, Qingdao University of Science and Technology, Qingdao, China.


*Domestic
See the annual report in Japanese (22 articles)

**Awards**
1. Mayu Suda, Sol–gel-derived silica–(Gd,Pr)PO$_4$ transparent glass-ceramics applicable to narrow-band UVB phosphors, Young Scientist Presentation Award, The 9th International Symposium on Inorganic Phosphate Materials, ISIPM-9, Sep. 25-28, 2016, Tokyo Metropolitan University, Tokyo
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Doctor’s course -1
Master’s course -13
Bachelor 4-8

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,
ligh t harvesting type energy transfer was realized.

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,
thermovigrammetric 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. Research on Transparent Clay Membrane Systems
Shinsuke TAKAGI, Tetsuya SHIMADA

Cationic porphyrin was successfully intercalated into
transparent clay membrane by developing the new strategy for
the sample preparation conditions. When water : ethanol = 1 : 2
was used as solvent for porphyrin penetration process,
high density intercalation of porphyrin into the clay membrane
was achieved. In the interlayer space, porphyrin molecules do
not aggregate owing to inter-charge distance matching effect
(size-matching effect), even at high density condition.
Judging from XRD and absorption measurements, the
orientations of the porphyrins in the clay layers should be
almost parallel to the clay nanosheet as monolayer. Because the
fluorescence quantum yield did not depend on its loading level,
it is turned out that intercalated TMPyP in the clay film keeps
the photo-activity even under the high density conditions.
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.

Papers with Peer Review


Books


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

Invited Lectures


+1 article in Japanese (See the annual report in Japanese)

Academic Meeting

International

1. A construction of artificial light-harvesting system with energy migration functionality of xanthene derivative on the inorganic nano-sheet, Y. Ohtani, T. Shimada, S.
Reports from Research Groups

1. Takagi, XXVIth IUPAC Symposium on Photochemistry, Osaka (Japan), April, 2016.

Domestic
See the annual report in Japanese (40 articles)

Awards
7. Masahiro TABUCHI, Summer seminar of Forum on Low-dimensional photofunctional Materials, Excellent Poster Award, September, 2016.
9. Keito SANO, 2017 International Conference on Artificial
Yamaguchi Laboratory

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Master’s course -6
Bachelor 4 -2 (Foreign student 1)

■Outlines of the Research
1. Development of Photofunctional Ruthenium Complexes
Motowo YAMAGUCHI
a) Switching function of ligand photodissociation: New mixed-ligand type ruthenium complex with a terpyridine-type ligand derivative having imidazolyl groups which was reversibly protonated and deprotonated by acid and base has been synthesized and the control of its ligand photodissociation reaction has been examined. The reversible protonation and deprotonation was affirmed, then the ligand photodissociation reaction has been examined in acetone. It was found that the rate of photo-induced dissociation reaction 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 introduced to the terpyridine-type ligand of the complex 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.

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 moiety as the unit, we have found that the macrocyclic trinuclear, molecular triangle, and tetranuclear complexes, molecular square were effectively obtained by self-assembly. We have already reported that two molecules of aromatic compound were included in the cavity of molecular square. This time, we found that two molecules of cationic anthracene amide derivatives were included. Then the photodimerization of anthracene amide derivatives by visible light irradiation has been examined in the presence of the square, and the dimerization was found to be accelerated by the square up to TON more than 200. It was assumed that the square catalyzed the photodimerization as the sensitizer since anthracene derivative was not excited by visible light. It was revealed that the molecular square not only showed the inclusion behavior but also worked as the photocatalyst, that is, light-harvesting host.

d) Synthesis of 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. We have examined a variety of reaction conditions, and found out that the reaction in 2-methoxyethanol at 120 °C successfully gave rise to the macrocyclic tetranuclear ruthenium complex in good yield. It was found that a rod-like anion, such as a thiocyanate 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 1H NMR and DOSY spectra. Furthermore, electrochemical studies have been done by CV and DPV. It was found that the macrocyclic tetranuclear ruthenium complex was oxidized in three steps. In case of DPV studies in the presence of halide ion, it was revealed that the included chloride or bromide ion was protected from anodic oxidation.

2. Development of Novel Ionic Aggregation-Induced Emission and Solid-State Fluorophores
Kiyoshi SATO
Aggregation-induced emission (AIE) phenomenon has attracted great attention. Although a large number of AIE-active compounds based on Tang’s AIE fluorogens (AIEgens) have been reported in the last decade, most of them are neutral. Ionic
fluorophores have advantages for the design of AIEgens since their solubility and emission properties could be tuned by both of the cation and anion. In particular, changes of the counter ions would significantly influence the solid-state fluorescence, because the size and shape of counter ion and the interactions between ion-pair could affect the crystal packing structures. In this study, propeller-shaped pentaphenylimidazolium salts of five different counter anions were investigated as a novel ionic AIEgen and solid-state fluorophore. They show AIE activity with remarkable differences on their counter anions and anion-dependent solid-state fluorescence. These AIE-active and solid-state emissive ionic organic dyes have a promising feature for practical application as bio-imaging probes and energy-saving luminescent displays or light sources.

3. Synthesis and Properties of Polycyclic Azonia Aromatic Compounds by Multiple Photocyclization
Kiyoshi SATO

Nitrogen-doped graphenes have been the subject of recent attention because they exhibit good electro-catalytic activity for the oxygen reduction reaction of fuel cells. Polycyclic azonia aromatic compounds, in which some bridgehead carbon atoms are replaced by quaternary nitrogen atoms, represent a new class of N-doped graphenes with additional properties such as good solubility for polar solvents and high fluorogenicity. We have recently developed a facile synthetic strategy to prepare novel diazonia derivatives of hexabenzoperylene, a non-planar nano-scaled cationic N-doped graphene, by using multiple photo-induced dehydrocyclization of 1,2,6-triphenylpyridinium derivatives. In the present research, the photoreactions of the bis-bridged 1,2,4,6-tetraphenylpyridinium cations with alkyl chains (n = 2 and 3) and two dimethyl derivatives were newly investigated in order to clarify the scope and limitations of this reaction. The photo-irradiation to bis-ethylenbridged (n = 2) and N-(3,5-dimethyl)phenyl derivatives gave the bicycized photoproducts. In contrast, the reactions of the derivatives with longer alkyl chain bridged (n = 3) or 3,5-dimethyl on the pyridinium ring were terminated at monocyclization probably because the conformations of the monocyclized products are unfavorable for the second cyclization. In addition, when the irradiation time of the photoreaction of bis-ethylenbridged (n = 2) derivative was lengthened, unprecedented photo-dehydrogenation occurred and a seven aromatic ring fused compound was yielded as the final photoproduct. These reactions would be expected to be efficient synthetic methods for electro-active and luminescent organic materials.

Fig.4 Photobiscyclization of 1,2,6-Triphenylpyridinium Cations


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.

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.
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 diagnostic tool 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 urban site (Kagurazaka, Tokyo Science University) and suburban site (Minamisawara, Tokyo Metropolitan University). Characters (average concentration level, emission sources, contribution to ozone formation) of VOCs were compared at urban and suburban sites.

10. Measurements of atmospheric pollutants at mountain sites

Shungo KATO

Carbon monoxide, ozone, and sulfur dioxide 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.

11. HO lifetime and trace gas species measurements in sub-urban forest area

Shungo KATO

Hydroxyl radicals (OH) contribute to photochemical production of tropospheric ozone. OH lifetime (OH reactivity) and various trace gas species were observed at suburban forest area (FM-Tama), suburban of Tsukuba city, and suburban of Tokyo. Vertical distribution of trace gases were observed on the flux tower at forest area.

12. 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.

13. Application of biomass charcoal powder to stress resistance of proteins

Hidetaka NORITOMI

To reduce greenhouse gas emissions, biomass charcoal powder was prepared from forestry residues, which are carbon neutral, and was used as a protein carrier. We found that biomass charcoal powder 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. Fengming Chen, Luyao Lin, Jie Zhang, Ziyi He, Katsumi Uchiyama, Jin-Ming Lin

Single-Cell Analysis Using Drop-on-Demand Inkjet Printing and Probe Electrospray Ionization Mass Spectrometry


2. Jianmin Yang, Daisuke Katagiri, Sifeng Mao, Hulie Zeng, Hizuru Nakajima, Shungo Kato, Katsumi Uchiyama

Inkjet printing based assembly of thermostressive core-shell polymer microcapsules for controlled drug release


3. Jie Zhang, Fengming Chen, Ziyi He, Yuan Ma, Katsumi Uchiyama, Jin-Ming Lin

A novel approach for precisely controlled multiple cell patterning in microfluidic chips by inkjet printing and the detection of drug metabolism and diffusion

Analyt, 2016, 141, pp2940-2947

4. Shungo Kato, Yasuhiro Shiobara, Katsumi Uchiyama, Kazuhiiko Miuta, Hiroshi Okochi, Hiroshi Kobayashi, Shiro Hatakeyama

Atmospheric CO, O3, and SO2 Measurements at the Summit of Mt. Fuji during the Summer of 2013

Aerosol and Air Quality Research, 2016, 16, pp.2368-2377

5. Jie Zhan, Koji Furu, Hizuru Nakajima, Noriaki Kaneki, Ryoichi Ishimatsu, Koji Nakano, Toshihiko Imato, Akihide Hemmi

Development of a Portable Surface Plasmon Resonance Sensor with Multi-Sensing Points Based on the Linear CCD Sensor

Analytical Sciences, 2016, 32(6), pp.673-679

6. Hulie Zeng, Daisuke Katagiri, Tatsuke Ogino, Hizuru Nakajima, Shungo Kato, Katsumi Uchiyama

Droplet Enhanced Fluorescence for Ultrasensitive Detection Using Inkjet

Analytical Chemistry, 2016, 88 (12), pp 6135–6139

7. Hidetaka Noritomi, Shunichi Kurihara, Nobuyuki Endo, Satoru Kato, Katsumi Uchiyama
Effect of adsorption condition on thermal stability of proteins adsorbed onto biomass charcoal powder

8. Sifeng Mao, Chihao Sato, Yuma Suzuki, Jianmin Yang, Hulie Zeng, Hizuru Nakajima, Ming Yang, Jin-Ming Lin, Katsumi Uchiyama
Microchemical Pen: An Open Micromixer for Region-Selective Surface Modification
ChemPhysChem, 2016, 17, pp.3155-3159

The use of an inkjet injection technique in immunoassays by quantitative on-line electrophoretically mediated microanalysis

10. Xiangnan Dou, Yongzhan Zheng, Katsumi Uchiyama, Jin-Ming Lin
Fluorescent Carbon Nanoparticle: Mimic of Hydrogen Peroxide Property for Chemiluminescence System

11. Akihito Korenaga, Fengming Chen, Haifang Li, Katsumi Uchiyama, Jin-Ming Lin
Inkjet automated single cells and matrices printing system for matrix-assisted laser desorption/ionization mass spectrometry

12. Hidetaka Noritomi, Junpei Nishigami, Nobuyuki Endo, Satoru Kato, Katsumi Uchiyama
Organic solvent-resistant properties of proteins adsorbed onto biomass charcoal powder

OH Reactivity Measurement and Chemical Analyses of BVOCs Emitted from Sugi

Total OH reactivity measurement in a BVOC dominated temperate forest during a summer campaign, 2014
2016, Atmospheric Environment, 131, pp.41-54


Books
1. Katsumi Uchiyama
Generation of Ultra-small Droplets by an Inkjet and Its Application to Chromatography
Bunseki kagakou sougouronbunnenkantokusyu "super" vol.65, No.1, pp.1-11(2016)

2. Shungo Kato
Measurement of mountain ozone and carbon monoxide - Mt. Fuji-,
Ridai scientific forum, 2016 August (number 387).

■ Invited Lectures
1. Hulie Zeng, Daisuke Katagiri, Hizuru Nakajima, Katsumi Uchiyama
Droplet Enhanced Fluorescence for Ultrasensitive Detection Using 2 Inkjet
2016 China-Japan-Korea Symposium on Analytical Chemistry (CJK2016), K08

2. Katsumi Uchiyama
Analytical application of ink jet
Proc. of the 65th annual meeting of the Japan Society for Analytical Chemistry D1006* (in Japanese)

3. Katsumi Uchiyama
Nano/ Micro fabrication of chemical structure by micro chemical pen

• Academic Meeting

- International

1. O Daisuke Katagiri, Hulie Zeng, Hizuru Nakajima, Katsumi Uchiyama
Inkjet printing based assembly of thermoresponsive core-shell polymer microcapsules for controlled drug release
2016 China-Japan-Korea Symposium on Analytical Chemistry (CJK2016), Wuyi University, Wuyishan, China, P18

2. O Yong Zhang, Sifeng Mao, Hulie Zeng, Hizuru Nakajima, Katsumi Uchiyama
Synthesizing polymer lines with a microfluidic mixing-based chemical pen
2016 China-Japan-Korea Symposium on Analytical Chemistry (CJK2016), Wuyi University, Wuyishan, China, P12

3. O Weifei Zhang, Sifeng Mao, Jianmin Yang, Hulie Zeng, Hizuru Nakajima, Katsumi Uchiyama
The use of an inkjet injection technique in immunoassays by quantitative on-line electrophoretically mediated microanalysis (EMMA)
2016 China-Japan-Korea Symposium on Analytical Chemistry (CJK2016), Wuyi University, Wuyishan, China, P28

4. O Xiangnan Dou, Katsumi Uchiyama, Jinming Lin
Fluorescent Carbon Nanoparticle: Mimic of Hydrogen Peroxide Property for Chemiluminescence System
2016 China-Japan-Korea Symposium on Analytical Chemistry (CJK2016), Wuyi University, Wuyishan, China, P06

5. O Chiho Sato, Sifeng Mao, Hulie Zeng, Shungo Kato, Hizuru Nakajima, Katsumi Uchiyama
The development of micro-fluidic chemical pen for region selective modification
RSC Tokyo International Conference 2016, Makuhari-Messe, Chiba, C09

Organic Solvent Resistance of Proteins Adsorbed Biomass Charcoal Powder
Second International Conference on Science, Engineering
Development of Portable Fluorescence Detection System Using an Organic Photodiode Array Detector
PITTCON2017, Chicago, USA, 230-30P

**Domestic**
See the annual report in Japanese (30 articles)

**Awards**
1. Mao Asada (Master's course 2years)
   Student judge special prize
   Development of Surface Plasmon Resonance Sensor Using a DVD-R.
   Proc. of the 65th annual meeting of the Japan Society for Analytical Chemistry (Hokkaido University) (in Japanese)

2. Ryo Takahashi (Master's course 2years)
   Topics
   Development of Fluorescence Analysis System Using a Compact Disk-type Microfluidic Device and Its Application to Infection Disease Diagnosis
   Proc. of the 76th symposium of the Japan Society for Analytical Chemistry (Gifu Pharmaceutical University) (in Japanese)
Reports from Research Groups

Kubo Laboratory

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■ Outlines of the Research

1. 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 $\pi$-extended dibenzo-boron-dipyromethenes (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.

2. 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 $\pi$-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.

3. 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.

4. Visible Light-induced Water Splitting with Photosensitizing Dye
Name: Yuji Kubo and Yan J. 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 photoelectrochemical (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.

5. Synthesis of a 1-hydroxy-2,3,1-benzodiazaborine-containing $\pi$-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 increase 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.

6. 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-pinacolobenzyl oxy 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.

7. Synthesis of Tetraphenylethylene-Containing Boronate Macrocycles and their Self-Assembly
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, sequential dehydration of di(boronic acid)-appended tetraphenylethylene with dtrimethylolpropane was investigated.

Name: Yuji Kubo and Ryuehi Nishiyabu
Surface modification of a polyvinyl alcohol sponge with functionalized boronic acids to develop porous materials applicable for multicolor emission, chemical sensing and 3D cell culture.

Papers with Peer Review

Book Chapter
See the annual report in Japanese for other book chapter (one chapter).

Invited Lectures
See the annual report in Japanese for other invited lectures (two presentations).
2. Materials, medicine and energy: measuring the versatility of metal complex, J. Yan Mulyana,11th Joint Conference of Chemistry in conjunction with the 4th Regional Biomaterials Scientific Meeting, Plenary Session II, Purwokerto, Central Java, Indonesia, 16 September 2016.

Academic Meeting
International

Domestic
See the annual report in Japanese for other presentations (16 presentations).
1. Photoelectrochemical water splitting using organic dyes, O. Suryani ・Y. Mulyana ・Y. Kubo, 3A06, Annual Meeting on Photochemistry 2016, The University of Tokyo (Komaba Campus), Tokyo, 2016, Sep 8th
2. New ruthenium complex for dye-sensitized photo electrochemical water splitting, I. Purnama, Y. Mulyana, Y. Kubo, 3P075, Annual Meeting on Photochemistry 2016, The University of Tokyo (Komaba Campus), Tokyo, 2016, Sep 8th
3. Organic and inorganic materials for light-powered hydrogen production from water, Y. Mulyana, Y. Kubo, 3A07, Annual Meeting on Photochemistry 2016, The University of Tokyo (Komaba Campus), Tokyo, 2016, Sep 8th
4. Water-Dispersible Boronate Microparticles for Aiming at Preparation of Chemosensors with Multicolor Fluorescence Emission, PRATOMO Uji ・NISHIYABU Ryuhei ・KUBO


■ Patents
See the annual report in Japanese (6 patents).

■ Awards
Shishido Laboratory

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**Outlines of the Research**

1. Development of supported alloy nanoparticle catalysts effective for hydrogen storage-evolution cycles  
   Tetsuya Shishido, Hiroki Miura

   Recently, hydrogen fuel battery attracts much attention thanks to its high energy efficiency. Therefore, hydrogen carrier systems enable safe and stable transportation of hydrogen. In this year, we investigated hydrogeneration of ammonium hydrogen carbonate/dehydrogenation of ammonium formate reversible system, and found that supported PdAu alloy catalysts showed high activity. Furthermore, these catalysts were also effective for methanolysis ammonia borane. Spectroscopic investigation revealed charge transfer from Pd to Au, and coordination environment around Pd atom of PdAu alloys remarkably affected their catalytic activity.

2. Metal-oxygen 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 characterization and catalytic performance of nickel aluminate-based catalysts (NiAl2O4), which possess a high surface area and thermal stability. The catalytic activity was evaluated using test reactions of NO, CO, and C3H8 under various simulated exhausts with different air-to-fuel ratios. As a result, NiAl2O4 showed moderate NO reduction activity in a wide oxygen concentration. The isolated hexacoordinated Ni of NiAl2O4 can react with NO without redoxant agent. Supported Pd promote Ni2+ reduction to Ni metal and the Cu in NiAl2O4 activated CO oxidation.

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 benzamide to internal alkynes to give isoindolinone derivatives. Under optimized conditions, a series of isoindolinones were obtained in good to high yields. Furthermore, we also found that supported PdAu catalysts were effective for hydrosilylation of internal alkynes, unsaturated ketones and allenes under mild reaction conditions to afford the corresponding organosilicon compounds in high yields.

**Papers with Peer Review**


4. Intermolecular [2+2+1] Carbonylative Cycloaddition of Aldehydes with Alkynes, and Subsequent Oxidation to...


Invited Lectures
3. “Selective molecular transformations by supported alloy nanoparticle catalysts; Hydrosilylation by supported PdAu catalysts as an example.” Tetsuya Shishido, Aug 24, 2016, Oita University.
5. “Structure and catalysis of supported alloy nanoparticles; Dehydrogenation over Pt-Sn alloy catalysts” Tetsuya Shishido, 9th ESICB symposium, Oct 31, 2016, Kyoto University.
7. “Development of oxide-supported Ru catalysts directed toward synthesis of useful chemicals” Hiroki Miura, JPIJS meeting in east division, Dec 9, 2016, Seikei University.
8. “Structure and catalysis of supported alloy nanoparticles; selective molecular transformation and hydrogen evolution” Tetsuya Shishido, 2016 3rd lectureship on research centre for artificial synthesis, Feb 2, 2016, Osaka City University.

Academic Meeting
International
4. 1,4-hydrosilylation of unsaturated ketones over supported PdAu catalysts, K. Endo, R. Ogawa, H. Miura, T. Shishido, 6th IUPAC International Conference on Green Chemistry (ICGC-6), September 4-8, 2016, Venezia, Italy

Domestic
See the annual report in Japanese (32 articles)

Awards
1. Poster Award “Hydrosilylation of alkenes by supported PdAu alloy catalysts” Ryoichi Ogawa, Keisuke Endo, Hiroki Miura, Tetsuya Shishido, 14th Catalyst workshop in Fujisawa, August 1, 2016, Fujisawa.
2. Poster Award “Dehydrogenative coupling of alcohols by supported Cu catalysts” Karin Nakahara, Hiroki Miura, Tetsuya Shishido, 14th Catalyst workshop in Fujisawa, August 1, 2016, Fujisawa.
3. Excellent Poster Award “Hydrosilylation of internal alkenes by supported PdAu alloy catalysts” Ryoichi Ogawa, Keisuke Endo, Hiroki Miura, Tetsuya Shishido, 6th CSJ chemistry festa 2016, November 11, 2016, Funabashi.