









GIGAKU TECHNO PARK BANGKOK







### Background

The collaboration between Chulalongkorn University (CU) and Nagaoka University of Technology (NUT) was first established by Department of Materials Science on the individual basis. After that, on 2006, Faculty of Science, CU and Faculty of Engineering, NUT has first signed the official agreement of academic and educational collaboration. Since then, the collaboration with NUT has been expanded to other departments, such as Departments of Chemistry, Biochemistry. Until now, more than 20 students of Faculty of Science, CU have participated in the short-term and long-term student exchange programs with NUT. The double doctoral degree program agreement between Faculty of Science, CU and Faculty of Engineering, NUT has been established since 2013 to confirm our strong and on-growing relation between the two universities.

The 1<sup>st</sup>, 2<sup>nd</sup> and 3<sup>rd</sup> Joint symposium CU-NUT (supported by Chula Global Network) was successfully organized by Departments of Chemistry, Biochemistry and Materials Science, CU and Faculty of Engineering, NUT and in 2010, 2012 and beginning of 2015, respectively, with the purposes to exchange the research results and discussion among the experts in various fields and to accelerate the collaborations between Thai and Japanese scientists in both institutions. Thus, on October 21, 2015, Departments of Chemistry, Biochemistry, Materials Science, Environmental Engineering and Chemical Engineering, CU will host the 4<sup>th</sup> Joint Symposium CU-NUT at Chulalongkorn University to present, exchange and discuss the scientific results and further strengthen the collaborations among CU and NUT professors on the two main topics: (i) Chemistry, Materials Science and Technology and (ii) Biochemistry and Environmental Engineering. This symposium will in turn be beneficial toward the development of the double doctoral degree program between CU and NUT. Furthermore, the Opening Ceremony of CU-NUT Gigaku Techno Park Office, which will be used as a coordination center to establish and expand the CU-NUT research collaborations to industrial sectors in Thailand, Japan and ASEAN countries, will also be held on October 22, 2015 at Faculty of Science, CU.





## Program for 4<sup>th</sup> Joint Symposium CU-NUT & Opening Ceremony of CU-NUT Gigaku Techno Park Office

October 21, 2015: 4 <sup>th</sup> Joint Symposium CU-NUT		
	Locatio	on: Room 1119, 11 <sup>th</sup> Floor, MHMK Building
Time		Activity
09.00-09.20		Opening and Welcome Remarks
		Assoc.Prof. Dr. Polkit Sangvanich
		Dean of Faculty of Science, CU
Technical Session I: Chemistry, Materials Science and Technology		
09.20-09.40	(0-01)	Active Utilization of CU-NUT GIGAKU Core to Research
		Networking in Sustainable Green Materials for Future
		Collaboration
		Prof. Takaomi KOBAYASHI
		Department of Materials Science and Technology, NUT
09.40-10.00	<b>(O-02)</b>	Diuron Degradation via Photocatalytic Reaction in a
		Microreactor
		Assoc. Prof. Dr. Varong PAVARAJARN
		Department of Chemical Engineering, CU
10.00-10.20	<b>(O-03)</b>	Application of Ceria-Based Lanthanides to Photoelectrocatalysis
		and Electrochemical Oxidation of Methane
		Prof. Kazunori SATO
		Department of Materials Science and Technology, NUT
10.20-10.40	<b>(O-04)</b>	Effect of Non-Stoichiometry on Electrical Properties of Barium
		Strontium Titanate Ceramics
		Dr. Natthaphon RAENGTHON
		Department of Materials Science, CU
10.40-11.00		Coffee Break







11.00-11.20	<b>(O-05)</b>	Applications of Atmospheric Discharge Plasm
		Prof. Nobuhiro HARADA
		Department of Electro, electronics, information, NUT
11.20-11.40	<b>(O-06)</b>	Effect of Gas Sparger and Plastic Media on Mass Transfer and
		Hydrodynamic Parameters in Airlift Reactor
		Prajak SASTARAVET
		Department of Environmental Engineering, CU
11.40-12.00	<b>(O-07)</b>	Organic-Inorganic Nanomatrix Structure of Natural Rubber
		Assoc. Prof. Seiichi KAWAHARA
		Department of Materials Science and Technology, NUT
12 00 13 30		I unch (MHMK Lobby Ground Floor)
12.00-13.30		Lunch (Millivik Lobby, Glound Piool)
Technical Ses	sion II:	Biochemistry & Environmental Engineering
10 00 10 50		
13.30-13.50	( <b>O-08</b> )	Crystal Structure of Yeast D-Aspartate Oxidase
13.30-13.50	( <b>O-08</b> )	Crystal Structure of Yeast D-Aspartate Oxidase Assoc. Prof. Shoji TAKAHASHI
13.30-13.50	( <b>O-08</b> )	Crystal Structure of Yeast D-Aspartate Oxidase Assoc. Prof. Shoji TAKAHASHI Department of Bioengineering, NUT
13.30-13.50 13.50-14.10	(O-08) (O-09)	Crystal Structure of Yeast D-Aspartate OxidaseAssoc. Prof. Shoji TAKAHASHIDepartment of Bioengineering, NUTSolid Degradation of Biomass in Anaerobic Digestion
13.30-13.50	(O-08) (O-09)	Crystal Structure of Yeast D-Aspartate OxidaseAssoc. Prof. Shoji TAKAHASHIDepartment of Bioengineering, NUTSolid Degradation of Biomass in Anaerobic DigestionSupachai HIRUNSUPACHOTE
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13.30-13.50 13.50-14.10 14.10-14.30 14.30-14.50	(O-08) (O-09) (O-10) (O-11)	Crystal Structure of Yeast D-Aspartate OxidaseAssoc. Prof. Shoji TAKAHASHIDepartment of Bioengineering, NUTSolid Degradation of Biomass in Anaerobic DigestionSupachai HIRUNSUPACHOTEDepartment of Environmental Engineering, CUGenome Database Mining for Genes Encoding MonolignolPrecursor Conversion EnzymesAsst. Prof. Naofumi KAMIMURADepartment of Bioengineering, NUTPerformance of Nitrate Reduction in Fluidized Bed Reactorwithout Internal Recirculation
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# 14.50-15.10(O-12)Impact of Nanoscale-Zero Valent Iron (Nzvi) on Environmental<br/>Microorganisms: Membrane Damage and Bacterial Adaptive<br/>Response

Panaya KOTCHAPLAI

Department of Biochemistry, CU

15.10-15.30		Coffee Break
15.30-17.30	Poster Presentation and Discussion	
	( <b>P-01</b> )	Gigaku Techno Park a Newly Developed Model of
		Academia-Industry- Government Cooperation
		Adjunct Prof. Dr. Akio Takahashi, Gigaku Techno Park, NUT
	( <b>P-02</b> )	Analysis of Lipid Production in the Oleaginous Yeast
		Rhodosporidium Toruloides
		Atsushi Miyata, Department of Bioengineering, NUT
	( <b>P-03</b> )	Analysis of the Transglycosylation Activity of BGLII in
		Trichoderma Reesei
		Ayana Nakamura, Department of Bioengineering, NUT
	( <b>P-04</b> )	Identification of the Uptake System for Lignin-Derived
		Aromatic Compounds in <i>Sphingobium</i> sp. Strain SYK-6
		Kosuke Mori, Department of Bioengineering, NUT
	( <b>P-05</b> )	Transcriptional Regulation of the Vanillate and Syringate
		Catabolic Genes in Sphingobium sp. Strain SYK-6
		Takuma Araki, Department of Bioengineering, NUT
	( <b>P-06</b> )	Whole Genome Determination of Acinetobactor Baylyi Strain
		GFJ2
		Michiro Tabata, Department of Bioengineering, NUT
	( <b>P-07</b> )	Influence of Microwave Radiation for Curing the Fly Ash and
		Aluminium Hydroxide Waste Based Geopolymer
		Sujitra Onutai, Department of Materials Science and Technology,
		NUT







( <b>P-08</b> )	Polysaccharide Porphyran Extracted from Discolored Laver
	and its Application to Moisturizing Agent
	Takumi Saito, Department of Materials Science and Technology,
	NUT
( <b>P-09</b> )	Green Chemicals Calixarene Hosts Synthesized for Highly
	Selective Fluorescence Chemo Sensor for Pb <sup>2+</sup>
	Lisa Nakajima, Department of Materials Science and Technology,
	NUT
( <b>P-10</b> )	Latex-State NMR Spectroscopy for Analysis of
	Prevulcanization of Isoprene Rubber Latex
	Kewwarin Sae-Heng, Department of Materials Science and
	Technology, NUT
( <b>P-11</b> )	Preparation and Properties of Phenyl-Modified Natural
	Rubber
	Nuorn Choothong Department of Materials Science and
	Technology, NUT
( <b>P-12</b> )	Crystallization Behavior of Sodium Iron Pyrophosphate Glass
	Chihara Akatsuka, Department of Materials Science and
	Technology, NUT
( <b>P-13</b> )	Synthesis of Glass-Ceramics Containing High Dialectic
	$Bi_{1.5}ZnNb_{1.5}O_7$ Nanocrystals and Investigation of their Physical
	Properties.
	Keisuke Shimamura, Department of Materials Science and
	Technology, NUT
( <b>P-14</b> )	Lanthanide Extraction from Ores
	Amnart Sukpia, Department of Chemistry, CU
( <b>P-15</b> )	Fabrication of Pt/TiO <sub>2</sub> Composite Nanofibers by Sol-Gel
	<b>Reaction combined with Electrospinning Method</b>
	Kannanut Seneekatima, Department of Materials Science, CU





### (P-16) Electrical Conductivity of Ca-, Co-Doped PrSr<sub>3</sub>Fe<sub>3</sub>O<sub>10-δ</sub> for IT-SOFCs

Wichuma Jiraroj, Department of Chemistry, CU

 (P-17) Controlling Color Transition of Polydiacetylene/Zinc Oxide Nanocomposites Dispersed in Toluene by Varying Alkyl Chain Length of Cationic Surfactant

Supakorn Seetha, Department of Materials Science, CU

- (P-18) Biotransformation of Solar Energy and into CO<sub>2</sub> Bioplastic
  Polyhydroxybutyrate (PHB) by Photosynthetic Cyanobacteria
  Tanakarn Monshupanee, Department of Biochemistry, CU
- (P-19) Biogradation Kinetics of Oranophosphate Insecticide by *Pseudomonas Plecoglossicida* PF1
   Tipsuda Subsanuan, Department of Biochemistry, CU







# **October 22, 2015:** Opening Ceremony of CU-NUT Gigaku Techno Park Office **Location:** Room 1208/9, 12<sup>th</sup> Floor, Maha Vajirunhis Building

Time	Activity		
	<b>Opening Remarks I</b>		
10.00-10.10	Prof. Dr. Mongkol TECHAKUMPHU		
	Vice President, Chulalongkorn University (CU)		
10.10-10.20	<b>Opening Remarks II</b>		
	Prof. Nobuhiko AZUMA		
	President, Nagaoka University of Technology (NUT)		
	<b>Opening Remarks III</b>		
10.20-10.30	Mr. Akihiko UCHIKAWA		
	Minister-Economic Section, Embassy of Japan in the Kingdom of Thailand		
	Welcome Remarks		
10.30-10.45	Assoc. Prof. Dr. Polkit SANGVANICH		
	Dean, Faculty of Science, CU		
	Super Global University Project: CU-NUT Gigaku Techno Park		
10.45-11.00	Prof. Dr. Takaomi KOBAYASHI		
	Gigaku Techno Park Organizing Committee, NUT		
11 00 11 10	Coffee Breek and Networking		
11.00-11.10	Confee Break and Networking		
	E-ASIA Program		
11.10-11.20	Ms. Eriko KISHIDA		
	E-ASIA Special Program Coordinator		
	E-ASIA JRP Secretariat/Japan Science and Technology Agency (JST)		
	<b>CU-NUT-Industrial Collaborations I</b>		
11.20-11.35	Asst. Prof. Dr. Sirithan JIEMSIRILERS		
	Deputy Dean, Faculty of Science, CU		





	<b>CU-NUT-Industrial Collaborations II</b>	
11.35-11.50	(1) Mr. Kazumasa MIZUMO, Managing Director of Thai Fukuda Co., Ltd.	
	(2) Mr. Tetsuro NOZAKI, President of Nippon Seiki Co., Ltd.	
11.50-12.00	<b>Ribbon Cutting @ CU-NUT Gigaku Techno Park Office (11<sup>th</sup> Floor)</b> Photo Session and Press Interview	
	<b>Opening Celebration</b>	
	@ Dipak C. Jain Room, Sasa International House,	
12.00 -14.00	Chulalongkorn University	
	(Closing Remarks by Prof. Dr. Supot Hannongbua,	
	Former Dean, Faculty of Science, Chulalongkorn University)	

# ABSTRACTS OF ORAL PRESENTATIONS

#### Active Utilization of CU-NUT GIGAKU Core to Research Networking in Sustainable Green Materials for Future Collaboration

Takaomi Kobayashi

Department of Materials Science and Technology, Nagaoka University of Tecnonolgy, 1603-1 Kamitomioka, Nagaoka, 940-2188, Japan (\*takaomi@nagaokaut.ac.jp)

As environmental concerns increase, people are looking beyond their internal operations to improve the environmental profile of their products from their origins in raw inputs through their lifetimes in use by customers. Nowhere is this more essential than for cutting edge of Sustainable Green materials in CU-NUT projects of producing green products. Understanding and mitigating GIGAKU impacts, Science of technology is attractive and meaningful for our global mitigation, and as an opportunity for competitive differentiation. As based upon strategies and concepts aimed at both universities, interdisciplinary project to Form a Hub for Global Human Resources Development and New Industry Creation-Building a sustainable society through highly interactive, cooperative educational research with Pacific Rim countries has been organized in green researches (2011-2015) and doctoral double degree program (DDP) has been established in CU-NUT by the Pacific Rim countries project in order to develop engineering education and research accelerating internationalization. Nowadays interdisciplinary education has been performed to upbring future researchers in the CU-NUT DDP program, especially for natural plant materials, waste fly ash utility and fuel cell. Thus, to reach this goal in sustainable green materials, here is ripple effects by the project goal achievement; 1) The project has enhanced practical abilities and enables advancement of studies in CU-NUT. 2) By providing global education in the field of green innovation from the early stage of graduate education, the possibility to foster practice-oriented doctors in the DDP program has been educating to students and staffs as a flexible international understanding and ideas, leading a sustainable society. 3) Particularly establishing in both universities enables response to globalization of practical education at graduate school. In the fields of biotechnology, environment, energy, and materials science for green innovation in green energy, as well as a mechanism of material and resource circulation, this program surly creates active circumstance of the collaboration. Also, the green innovation project can conduct basic technologies through research and development in both universities.

In future collaboration between both universities, it is quietly useful to utilize CU-NUT GIGAKU office in Chulalongkorn for our research stage. The GIGAKU Technopark (GTP) office, has just opened on October 22, 2015, is that CU-NUT Joint research developed cooperation of industry-university- government research in the foreign countries. In addition, upbringing of the practicing global engineer who responds to the social needs is promoted by supporting with the GTP support.

#### **O-02**

#### **Diuron Degradation via Photocatalytic Reaction in a Microreactor**

Rungthip Noisomran<sup>1</sup>, Worachate Khongthon<sup>1</sup>, Polkit Sangvanich<sup>2</sup> and Varong Pavarajarn<sup>1,\*</sup>

<sup>1</sup>Center of Excellence in Particle Technology, Faculty of Engineering, Chulalongkorn University, Bangkok, 10330 Thailand <sup>2</sup>Department of Chemistry, Faculty of Science, Chulalongkorn University, Bangkok, 10330 Thailand (\*Varong.P@chula.ac.th)

Diuron [3-(3, 4-dichlorophenyl)-1, 1-dimethyl urea] is a carcinogenic herbicide widely used in Thailand. Due to its persistence with half-life over 300 days in nature, diuron contamination becomes very serious environmental problem. In this work, the photocatalytic degradation of diuron in a microreactor is investigated. Not only the kinetics of the degradation is investigated, the involvement of light on the degradation pathway is also reported. Degradation intermediates formed under exposure of light and those formed without the need of light are systematically investigated. Due to chemical stability of diuron, degradation via photolysis is negligible. On the other hand, when P25 titanium dioxide is present as a photocatalyst in the system, significant degradation is observed. It was found that mass transfer resistance in the reactor could be neglected as long as the thickness of the channel is smaller than 500 µm. Most intermediate products are associating with the attack by hydroxyl radical at various functional groups in the diuron molecule. It is interesting to observe that new intermediates are formed when the center part of the reactor is masked. Without the light, hydroxyl radicals are not generated. Therefore, the results suggest that the intermediates firstly formed by the photocatalytic degradation of diuron in the first section of the reactor, where it was exposed to light, can interact further with each other, with water, or with hydroxyl ion to form other intermediates without the assistance of light. The reactions that can take place without the light include elimination of methyl group from the aliphatic part of the molecule, hydroxylation of the aliphatic functional groups and conjugation of the intermediates to form larger molecule.

#### Application of Ceria-Based Lanthanides to Photoelectrocatalysis and Electrochemical Oxidation of Methane

Kazunori Sato

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Oxides containing elements from the lanthanide series, lanthanum to gadolinium in practical, are a group of compounds whose unique electronic and ionic properties allow useful applications to catalysts, catalyst support, solid electrolyte, etc. We have been focusing on ceria-based lanthanides as a metal oxide semiconductor for removal of heavy metal ions in aqueous solutions by photoelectrodeposition and reduction of carbon dioxide by photoreduction and an oxide-ion conductor for an application to a cermet anode, which makes possible for the direct use of methane in solid oxide fuel cells [1, 2]. For the removal of hazardous heavy metal ions, the photoelectrodeposition effect has been investigated for  $(CeO_2)_{1-X}$   $(Ln_2O_3)_X$  (Ln = La, Sm, Gd) crystalline particles. These materials have been investigated as a photoelectrocatalyst for the reduction of carbon dioxide dissolved in water and formation of methane as a product. Ceria-based oxides have been also investigated for an enhancement of the direct oxidation of methane as a component of the cermet anode combined with a ceria-based oxide electrolyte, the effect of which is combined with a sufficient oxide ion supply through the electrolyte. These effects will be discussed in terms of not only the microstructure but also the band structure calculation.

#### Reference

- [1] J. Ayawanna, W. T. Teoh, S. Niratisairak, K. Sato, *Mater. Sci. Semicond. Process.*, 40 (2015) 136-139.
- [2] K. Sato, H. Tsuchiya, W. T. Teoh, J. Ayawanna, Sensors & Mater., in press.

#### Effect of Non-Stoichiometry on Electrical Properties of Barium Strontium Titanate Ceramics

Ratchanin Wanichakulviriya<sup>1,2</sup>, Sirikarn Paechotrattanakul<sup>1,2</sup>, Hansa Pasdu<sup>1,2</sup>, Naratip Vittayakorn<sup>1,2</sup> and Natthaphon Raengthon<sup>3,\*</sup> <sup>1</sup>Department of Chemistry, Faculty of Science, King Mongkut's Institute of Technology Ladkrabang, Bangkok, 10520, Thailand <sup>2</sup>Advanced Materials Research Unit, Faculty of Science, King Mongkut's Institute of Technology Ladkrabang, Bangkok, 10520, Thailand <sup>3</sup>Department of Materials Science, Faculty of Science, Chulalongkorn University, Bangkok, 10330, Thailand (\*Natthaphon.R@chula.ac.th)

Barium titanate-based perovskites are commonly used in electronic applications such as multilayer or thin film ceramic capacitors and piezoelectric devices. Several techniques can be used to modify the materials to improve their properties such as microstructure engineering, powder synthesis techniques, composition controls, dopant addition, and controlling stoichiometry, for example. In this study, Barium strontium titanate, (Ba,Sr)TiO<sub>3</sub>, which is commonly used for capacitor applications, was selected to investigate electrical properties after modification by controlling stoichiometry of the materials. The excess and deficient of Ba- and Sr-cations were studied. Dielectric properties are not significantly affected by changing stoichiometry of the materials, which is similar to phase transition of the materials. However, high-field dielectric response showed significant effect after modification by controlling stoichiometry of the materials as seen by ferroelectric behavior. Discussion of possible mechanisms that explain the change in ferroelectric behavior will be provided.

#### **Applications of Atmospheric Discharge Plasma**

Nob. Harada<sup>\*</sup>, Takashi Kikuchi, Toru Sasaki and Kazumasa Takahashi Plasmadynamics Laboratory, Nagaoka University of Technology, 1603-1 Kamitomioka, Nagaoka 940-2188, Japan (\*nob@nagaokaut.ac.jp)

Recently, applications of plasma produced by electric discharges at atmospheric pressure have been widely studied. Main application areas are surface treatment, surface coating, water and/or gas treatments, environmental-, bio- and medical applications. If atmospheric discharge plasma (ATMDP) was used, vacuum vessel and pumping system are not required. Furthermore, in-line and continuous processing are possible. Experimental set up is also simple as shown in Fig.1. Facility consists of high-voltage power supply and plasma reactor with diagnostic equipment. Comparison of before and after treatment is important using such as SEM, XPS for surface observation, water/gas analyzer and so on. Cost of facility is not so high an operating cost is only electric power for processing and additional gas if required.

Major expected effects of ATMDP are; 1) accelerated charged particles of both ions and electrons impacts, 2) chemical reactions caused by highly activated radicals and molecules such as  $O^-$ ,  $OH^-$ ,  $O_3$ , etc. which are produced in the gas by charged particle collisions, and 3) light emitted from the plasma in the UV regime.

So far, we have tried surface cleaning and enhancement of wettability of glass plate to improve following processing such as painting, adhesion, etching, and so on. Thin wire annealing was also effectively achieved using ATMDP. Gas and water treatment can be studied and some application to supply purification of water has already in commercialization. Recently, application field has been extended to bio-medical field. Inactivation of micro-organisms was

studied in order to solve so-called ballast water problem. Our laboratory has just started international collaboration for this application study of ATMDP with UTCC, Bangkok and HCMUTE, Ho Chi Minh city, Vietnam. Latest activities will be presented at the joint symposium.



Fig. 1 Typical experimental set up of surface treatment with atmospheric discharge plasma.

#### Effect of Gas Sparger and Plastic Media on Mass Transfer and Hydrodynamic Parameters in Airlift Reactor

Prajak Sastaravet, Rewadee Dammee, Passaworn Warunyuwong, Nawaporn Thaphet, Kritchart Wongwailikhit, Kasidit Phanpa ,Narapong Hongprasith, Nattawin Chawaloesphonsiya, Marupatch Jamnongwong and Pisut Painmanakul\* *Chulalongkorn University, Bangkok 10330, Thailand; Tel: (089)-920-4257, Fax : (662)-218-6666* (\*pisut114@hotmail.com)

The aim of the present article is to know the absorber model as well as to understand the dynamic behavior of absorption process. The purpose of this work intended to study the effect of sparger sizes and plastic media shapes in an internal airlift reactor (IALR) on the oxygen absorption to tap water. The advantages of *IALR* are easy to operate, low maintenance requirements, simple construction, absence of moving parts and high mass transfer rate. It was found that bubble diameters depended on the types of sparger between rigid and wood sparger. The rigid sparger has higher specific interfacial area (a) and volumetric mass transfer coefficient (kLa) than wood sparger and also consumed lower power requirement than wood sparger. Moreover, it was found that increasing the solid plastic media, the polypropylene (PP) media, significantly enhanced the *kLa* coefficient due to the increase of *a*. This research also investigated the different shape and amount of *PP* plastic particles added into the reactor. The results showed that the ring shape media was the optimal media because of providing the high kLa coefficient and a due to its capability to trap bubbles in its hollow. Additionally, the influences on mass transfer parameter (kLa) and bubble hydrodynamic parameters (gas holdup;  $\varepsilon g$ , bubble diameter; dB, bubble rising velocity; UB and a) were determined in this work.

#### References

[1] P. Painmanakul, K. Loubiere, G. Hebrard, and P. Buffiere, Chem Eng Process 43, Study of different membrane spargers used in waste water treatment: characterisation and performance, (2004) 1347–1359

[2] P. Painmanakul and G. Hebrard, Chem Eng Process 61, Effect of surfactants on liquid-side mass transfer coefficients in gas–liquid systems: A first step to modeling, (2006) 6249–6260.

#### **Organic-Inorganic Nanomatrix Structure of Natural Rubber** Seiichi KAWAHARA<sup>\*</sup>

Department of Materials Science and Technology, Nagaoka University of Technology 1603-1 Kamitomioka-cho, Nagaoka, Niigata, 940-2188, JAPAN Tel: +81-258-47-9301, Fax: +81-258-47-9300 (\*kawahara@mst.nagaokaut.ac.jp)

Organic–inorganic nanomatrix composite is a novel nanocomposite, which conflicts with the conventional wisdom of a multi-component system with the island-matrix structure, which consists of both major components as the matrix and minor components as the dispersoid. It is difficult to realize an antithesis of the island matrix structure, which is a soft material consisting of a dispersoid of the major component and a matrix of the minor component. Thus, much attention has focused on developing novel nanocomposites using a nanomatrix less than several tens nm thick. Here, we define a nanomatrix composite as "a nanocomposite consisting of organic particles as the major component and organic or inorganic matrices as the minor component" [1]. In the present work, we use vinylethoxysilane as a vinyl monomer with an inorganic oxide precursor to form an organic–inorganic nanomatrix structure [2].

Figure 1 shows TEM images for the resulting grafted natural rubber (i.e., DPNR-graft-PVTES). The bright and dark domains in the TEM images of the as-cast film represent natural rubber and colloidal silica, respectively, because the films are not stained with a reagent. For the DPNR-graft-PVTES, the natural rubber particles (average diameter of about 1  $\mu$ m) are well dispersed into the silica nanomatrix as a



Figure 1 TEM image for DPNR-*graft*-PVTES.

three-dimensional nanonetwork. The nanonetwork consists of colloidal silica nanoparticles with diameters between 5 and 150 nm. The size of the colloidal silica depends upon both the vinyltriethoxysilane concentration and the initiator concentration. The stress strain curve for DPNR-graft-PVTES depends upon the vinyltriethoxysilane concentration.

[1] S. Kawahara, et.al., Polymer, 44 (2003) 4527.

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#### **Crystal Structure of Yeast D-Aspartate Oxidase**

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D-Aspartate oxidase (DDO) is an FAD enzyme that catalyzes the oxidative deamination of acidic D-amino acids but not of neutral and basic D-amino acids, which are substrates for D-amino acid oxidase (DAO). DDO has been isolated from various eukaryotic organisms. However, the structural features that provide the substrate specificity of DDO have not been fully elucidated, because the crystal structure of DDO was not reported. The yeast *Cryptococcus humicola* can produce a large amount of DDO (ChDDO) when D-aspartate is present in growth media. ChDDO plays a role in the assimilation and detoxification of acidic D-amino acids in the yeast and has some different enzymatic properties from those of animal ones; higher catalytic activity, higher specificity to D-aspartate and tighter cofactor-binding. The higher specificity to D-aspartate is valuable for the enzymatic determination and quantification of D-aspartate. In this study, to reveal the amino acid residues responsible for the substrate specificity of ChDDO, we determined its crystal structure.

ChDDO produced in *E. coli* was purified to electrophoretically homogeneity. The purified ChDDO was crystallized by the hanging drop method, and the crystal structure with D-aspartate was determined. Unlike to DAOs, ChDDO forms a homotetrameric ring-like structure through two head-to-head and two tail-to-tail interactions. The overall subunit structure of ChDDO is similar to that of DAOs: a nucleotide-binding Rossmann-fold in the tail side and the active site covered with a twisted antiparallel  $\beta$ -sheet and a loop (from Val232 to Thr242) termed active site lid. Similar to animal DAOs, the loop length was however much longer than that of a yeast DAO. In the active site, the  $\alpha$ -amino side chain of D-aspartate interacts with Gly344 and with Gln348 through a water molecule, and the  $\alpha$ -carboxy side chain interacts with Arg317 and Tyr245. These interactions are similar to those of DAOs. On the other hand, the  $\beta$ -carboxy side chain of D-aspartate interacts with Arg243 and His56 are suggested to play an important role in the substrate specificity of ChDDO.

#### Solid Degradation of Biomass in Anaerobic Digestion

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Solid biomass fermentation for biogas production is currently widely applied in Thailand. However, the biogas potential estimation is tested via BMP (bio-methane potential) test, which take long times about 45-60 days and has the cost for experiments. The modified model based on ADM1 model will reduce times and cost for this. The parameters in the model were studied from the bio-components of biomass and in the anaerobic reaction. This part was the study of solid remaining reduction correlated with biogas production. The chosen biomass was Napier grass fermented in various conditions compared with pure cellulose. The BMP test is done in vial bottle and the fermentation volume is 80 ml varying S/I ratio 60:40 and 90:10. The inoculum was seed from UASB plant. The Napier grass was grinded and separated to test in 2 sizes. The results found that grinded and not-grinded Napier grass/Inoculum in the ratio 60:40. The degraded solid was 52.36 and 50.59 % in 21 days. Ash content of remaining solid was 4.77, 9.64%. The accumulated biogas content was 66 and 86 ml. Anaerobic fermentation with S/I ratio 90:10 tested with grinded and not-grinded grasses. The degraded solid was 65.43, 30.28 in 12 days. Ash content of remaining solid was 17.44, 3.91%. The accumulated biogas content was 23 and 28 ml.

#### Genome Database Mining for Genes Encoding Monolignol Precursor Conversion Enzymes

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Modification of lignin composition and structure is an effective strategy to increase cell wall digestibility for biofuel production. Genes encoding enzymes that are capable of converting monolignol precursors would be useful to control the lignin biosynthesis. In this study, we focused on phenylpropenal double-bond reductases (DBR), which reduce the  $C\alpha$ -C $\beta$ -double bond of coniferyl aldehyde (CALD), an intermediate metabolite of the monolignol biosynthetic pathway. Reduction of CALD is expected to control the molecular weight of lignin in plant cell walls. Therefore we explored the genes encoding DBRs that exhibit higher activities than previously reported *Arabidopsis thaliana* DBR (At5g16970; Youn et al., 2006).

Putative DBR genes derived from nine different bacteria, the deduced amino acid sequences of which showed 39 to 45% identities with At5g16970, were selected from the NCBI microbial genome database. These genes in addition to At5g16970 were synthesized with codon optimization for the expression in *Escherichia coli*. Six DBR and At5g16970 gene products were finally obtained as purified enzymes. CALD conversion assays using purified DBRs indicated that only one DBR from *Parvibaculum lavamentivorans* (Plav) had a specific activity comparable to that of At5g16970. The optimal temperature and optimal pH of Plav were 40°C and 7.0, respectively. Plav preferred NADPH to NADH. Kinetic parameters,  $K_m$  and  $V_{max}$ , of the CALD conversion by Plav were determined to be 580  $\mu$ M and 1.2 U/mg, respectively. In order to improve the catalytic function of Plav, the amino acid substitutions on this enzyme were performed. As a result, we successfully obtained a mutant enzyme, which showed a five-fold higher catalytic efficiency ( $V_{max}/K_m$ ) than that reported for At5g16970.

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#### Performance of Nitrate Reduction in Fluidized Bed Reactor without Internal Recirculation

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In this study, the new configuration of Fluidized Bed Reactors (FBRs) with rubber granule as biofilm carrier media and operated without internal recirculation, was performed as an attached growth denitrification reactor. Due to a very low density rubber media and no recirculation, this new FBRs can operate under low hydraulic retention time (HRT) as 50 minutes. To investigate the denitrification efficiency, a synthetic nitrate-rich wastewater as 100 mg NO<sub>3</sub><sup>-</sup>-N/L with a varied COD concentration was fed to FBRs. Sodium nitrate and glucose were used as a NO<sub>3</sub><sup>-</sup> and carbon source to prepare this synthetic wastewater. The COD to nitrate ratio was varied as 1:1, 2:1, 3:1, 5:1 and 10:1.

The results show a very low performance for nitrate and COD at a ratio of 1:1 and 2:1 due to an insufficient of carbon source in denitrification process. On the other hands, at the ratio of 5:1 and 10:1, the results showed that the efficiency of nitrate removal was increased when the COD concentration increased. However, in these 2 ratios, the effluent contained nitrate lowers than 3 mg/L while high COD concentrations in effluent were still found. At ratio 3:1, the result showed the highest efficiency in both nitrate and COD removal as 93% and 89%, respectively. Moreover, both low nitrate and COD concentration as 7 mg NO<sub>3</sub><sup>-</sup>-N/Land 32 mg COD/L were found in the effluent in this ratio. It can be concluded that this FBRs showed a desirable performance at the ratio of COD to nitrate as 3:1. This ratio was lower than the ratio of 5:1 in a suspended growth denitrification.

Overall results of this study demonstrated that the FBR without internal recirculation using rubber granule as biofilm carrier media can achieve good performance of nitrate and COD removal at low HRT and low COD to nitrate ratio. This reactor provides the achievement of rapid and efficient biological denitrification process and can be considered as an alternative reactor for treating a nitrate rich wastewater.

**O-11** 

Impact of Nanoscale-Zero Valent Iron (nZVI) on Environmental Microorganism: Membrane Damage and Bacterial Adaptive Response Panaya Kotchaplai<sup>1,2</sup>, Eakalak Khan<sup>3</sup>, Nawaporn Vinayavekhin<sup>4</sup> and Alisa Vangnai<sup>2,5</sup>\* <sup>1</sup>International Program in Hazardous Substance and Environmental Management, Graduate School, Chulalongkorn University, Bangkok 10330, Thailand <sup>2</sup>Center of Excellence on Hazardous Substance Management (HSM), Chulalongkorn University, Bangkok 10330, Thailand <sup>3</sup> Department of Civil and Environmental Engineering, North Dakota State University, Dept. #2470, P.O. Box 6050, Fargo, ND 58108, USA <sup>4</sup>Department of Chemistry, Faculty of Science, Chulalongkorn University, Phayathai Rd, Bangkok 10330, Thailand. <sup>5</sup> Department of Biochemistry, Faculty of Science, Chulalongkorn University, Phayathai Rd, Bangkok 10330, Thailand. (\*Alisa.V@chula.ac.th)

Nanoscale-zero valent iron (nZVI) is a promising treatment agent for various contaminants due to its small size and high reactivity. However, the environmental impact of nZVI has also been concerned. In this study, *Pseudomonas putida* F1 was selected as the model microorganism. Exposure to nZVI significantly caused the reduction in cell viability; however, a rebound in cell number was observed after prolonged exposure. TEM analysis showed that nZVI heavily adsorbed onto bacterial surface and partially localized around bacterial membrane. Fatty acid profile analysis showed the significant conversion of *cis*- to *trans*-monounsaturated fatty acid upon nZVI exposure, resulting in the tightly packed bilayer, and more rigid membrane. It is likely that membrane rigidification is an adaptive response to counteract the membrane fluidizing effect of nZVI. This study unveils the significance of membrane damage as a toxicity mechanism of nZVI and bacterial adaptive response to nZVI exposure.

# ABSTRACTS OF POSTER PRESENTATIONS

#### Gigaku Techno Park, a Newly Developed Model of Academia-Industry-Government Cooperation

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Concept of GIGAKU Techno Park (GTP) is a "Global Fusion Campus" where not only students, researchers, but also engineers of companies both in Japan and counterpart country develop together the technological resolution to industry. This is clearly proactive attitude.

In particular, it is quite competitive and outstanding strategy that GTPs are deployed in most strategic areas where especially major Japanese industries including SMEs have been operating their production lines and technology marketing. During last two decades, many Japanese companies shifted their production lines to abroad in order to avoid relatively higher production costs. Even under recent devaluation of Yen, such a tendency still not changed. In addition, production volume of automobile sector in Japan has been decreased surprisingly. This is the evidence that Japanese companies now understand these area should be not for "assembly" anymore, but "consumer market" and "R & D".

Taking this tendency and change of markets, strategic collaboration among industry-SME, university and community in strategic areas should become more important for exploring new innovative markets and customers in the world. GTP is to provide a plat home for companies seeking business in particularly strategic industrial areas. At GTP global collaborative research, networking will be deployed among communities consisting of university, SME, private company, and government, so called ECO-SYSTEMS. Whatever SMEs need, such ECO-SYSTEMS will provide resolution. This networking may encompass business matching, collaborative research and access to human resources sector. Under strategic collaboration with Chulalongkorn University, we open CU-NUT GIGAKU TECHNO PARK. Newly developed collaboration among industry-academia-government in Thailand will demonstrate epoch making model to the society.



#### Analysis of Lipid production in the Oleaginous Yeast *Rhodosporidium Toruloides*

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In Japan, the degree of self-sufficiency in edible oil is only 3% and most of the edible oil is imported from abroad. However, the domestic oil production by the plantation of oleaginous plant is difficult in the small and narrow country of Japan.

Recently, the oleaginous yeast *Rhodosporidium toruloides* has received widespread attention. *R. toruloides* can produce high amounts of lipids (Triacylglycerol) from monosaccharide. In the optimal condition, lipid drop in *R. toruloides* cell occupy over 70% of dry cell weight. Lipids produced by *R. toruloides* have also a great potential to utilize for new energy resources. In addition, it is also possible to use these lipids as edible oils because the composition of lipids from *R. toruloides* is almost same of that of vegetable oil.

To carry out more effective lipid production by *R. toruloides* for industrial use, it is essential to elucidate lipid production mechanism of *R. toruloides*. In this study, the high lipid accumulating mutants were created and screened. Thereafter, their gene expression during lipid production was analyzed using microarray, and comparison of genomic DNA sequences of mutants to that of the wild type strain was performed.

*R. toruloides* was mutated by UV-irradiation and mutants accumulating high lipid were isolated by using cell sorter (SONY SH800) after lipids were stained by Nile Red. The candidates of the high lipid accumulating mutant were concentrated by repeating this process 3 times. After, they were cultivated in a 96-Well plate for 3days and optical density and fluorescence intensity were measured. Through this process, we succeeded to obtain two mutants accumulating high lipid content. The comparative transcriptome and genome analysis are in progress.

#### Analysis of the Transglycosylation Activity of BGLII in *Trichoderma Reesei*

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The filamentous fungus *Trichoderma reesei* is a potent producer of cellulase that is cellulolytic enzyme used to obtain glucose from cellulosic biomass. *T. reesei* produces cellulase when cultured on cellulose as a sole carbon source. Under cellulase producing condition, *T. reesei* produces 3 kinds of cellulase. They are cellobiohydrolase (CBH), endoglucanase (EG) and  $\beta$ -glucosidase (BGL). It has been thought that cellobiose which is degraded from cellulose with activities of CBH and EG, and sophorose which is formed from cellobiose by transglycosylation of BGL act as inducers of cellulase expression. Mutant strain PC-3-7 developed in Japan was derived from standard strain QM9414 by mutagenesis and acquired inducibility of cellulase on cellobiose as the substrate, and has higher productivity of cellulase than QM9414. Recently, it has been clarified that intracellular BGL (BGLII) of PC-3-7 is mutated. It is possible that BGLII function correlate with inducer formation for cellulase production. Therefore, in this study, we analyze the effect of mutation point of BGLII on its activity.

The gene encoding BGLII was cloned into the pET22b that is the expression vector of *Escherichia coli*. The codon of BGLII gene corresponding to the mutated amino acid in PC-3-7 was substituted into 20 amino acids. Resulting 20 vectors were introduced into *E. coli* BL21-codonplus, respectively. Expressed BGLII and its variants were purified and transglycosylation activity was analyzed. Consequently, wild type BGLII produced laminaribiose and cellotriose as well as unknown tetrasaccharide and pentasaccharide. Now, analysis of transglycosylation of BGLII variants is in progress.

**P-03** 

#### Identification of the Uptake System for Lignin-Derived Aromatic Compounds in *Sphingobium* sp. Strain SYK-6

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*Sphingobium* sp. strain SYK-6 is capable of utilizing various lignin-derived biaryls and monoaryls. The unique and specific degradation enzymes for various lignin-derived aromatics in SYK-6 would be suitable tools for the conversion of lignin into useful intermediate metabolites. To date, the catabolic enzyme genes for lignin-derived aromatics in SYK-6 have been extensively investigated. However, the uptake system for lignin-derived aromatic compounds remains largely unknown. In this study, we focused on the major facilitator superfamily (MFS) transporters, which are the largest known family proteins of secondary carriers in nature, and explored genes responsible for the uptake of 5,5'-dehydrodivanillate (DDVA), protocatechuate (PCA), vanillate (VA), syringate (SA), and ferulate (FA) from 67 putative MFS transporter genes in SYK-6.

The energy dependency of the uptake of DDVA, PCA, VA, SA, and FA by the cells of SYK-6 were initially investigated using a protonophore and an ATPase inhibitor. The results suggested that the uptake of these substrates mainly required a proton motive force. In order to determine the involvement of the 67 putative MFS transporter genes of SYK-6 in the uptake of lignin-derived aromatics, all of the putative MFS transporter genes were disrupted. Growth analysis of these mutants on DDVA, PCA, VA, SA, and FA showed that the disruption of ddvK resulted in a loss of the ability to grow on DDVA. Moreover, a *pcaK* mutant exhibited delayed growth on PCA. On the other hand, these mutants grew normally on other substrates. These results demonstrate that ddvK is responsible for the uptake of DDVA, and *pcaK* participates in the uptake of PCA. Since other 65 mutants grew normally on all the above substrates, other transporter systems or multiple MFS transporters appear to be involved in the uptake of VA, SA, and FA in SYK-6.

#### Transcriptional Regulation of the Vanillate and Syringate Catabolic Genes in *Sphingobium* sp. Strain SYK-6

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An understanding of both microbial catabolic genes for the degradation of lignin-derived aromatics and the transcriptional regulation of the catabolic genes is essential in establishing processes for effective utilization of lignin. *Sphingobium* sp. strain SYK-6 is a unique bacterium capable of utilizing various types of lignin-derived aromatics. In this study, we focused on the transcriptional regulation of the vanillate (VA) and syringate (SA) catabolic genes, including *desA*, *ligM*, and *desB*. The induction profiles of these genes were investigated, and *desB* promoter-binding proteins were characterized in order to uncover the transcriptional regulation system for the VA and SA catabolic genes.

The amount of transcripts of *desA*, *ligM*, and *desB* in SYK-6 cells grown in the presence or absence of VA or SA were quantified by qRT-PCR analysis. This analysis demonstrated that the transcriptions of all these genes were significantly induced in the cells grown in the presence of VA or SA. In order to identify the transcriptional regulator of desB, a desB promoter-binding protein was isolated and identified by peptide mass finger printing as DesR, a MarR-type transcriptional regulator. In order to determine the role of desR in the transcription of catabolic genes for VA and SA, desR in SYK-6 was disrupted. The resulting *desR* mutant grew significantly faster on VA and SA than the wild type. In addition, the amounts of transcripts of *ligM* and *desB* in *desR* mutant cells were significantly higher than those in the wild type. In contrast, the transcript amount of *desA* in the *desR* mutant was almost equal to the wild type. DNA binding analyses of DesR indicated that purified DesR bound to the promoter regions of *ligM* and *desB*, each of which contains a similar inverted repeat. On the other hand, the binding of DesR to the desA promoter region was not observed. These results indicate that DesR negatively regulates the transcription of *ligM* and *desB*, however, DesR dose not participate in the regulation of desA.

#### **P-06**

#### Whole Genome Determination of Acinetobactor Baylyi Strain GFJ2

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Acinetobactor baylyi strain GFJ2 degrades 4-chloroaniline, 3,4-dichloroaniline, and monohalogenated anilines [1]. To obtain the genome information of strain GFJ2, whole genome sequencing was performed using next generation sequencing method. 92,284 Single-End reads and 2,454,435 Mate-Pair reads generated by 454 GS-FLX Titanium (Rhoche) and MiSeq (illumina), respectively, were merged and assembled using de novo assembly software, Newbler, yielding total of 348 contigs and nine scaffolds. Sequencing gap was analyzed by GenoFinisher1.234 [2] and AceFileViewer1.13 [3] and gap sequences were amplified by PCR using GFJ2 total DNA as a template and sequenced by Sanger sequencing. Resultant sequence data were assembled with contigs or scaffolds by ATSQ bundled with GENETYX-MAC. GFJ2 genome was comprised of one chromosome (uncompleted; 3.4 Mb; 43.1%G+C) and total of seven plasmids (pGFJ1: 86 kb; 38.9%G+C, pGFJ2: 79 kb; 37.0%G+C, pGFJ3: 10 kb; 37.0%G+C, pGFJ4: 9.4 kb; 38.7%G+C, pGFJ5: 5.1 kb; 39.4%G+C, pGFJ6: 4.0 kb; 38.2%G+C, pGFJ7: 4.0 kb; 37.3%G+C). Annotation was performed using RAST Server [4]. Putative oxidoreductase and reductase that were responsible for dichloroaniline degradation were located on chromosome. One gap sequence containing two kinds of repeated contigs was not determined because of the lack of Mate-Pair reads and limitation of sanger sequencing length, that are to be sequenced by alternative method e.g. sequencing from library.

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#### Influence of Microwave Radiation for Curing the Fly Ash and **Aluminium Hydroxide Waste Based Geopolymer**

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Geopolymer is an alumino-silicate material which is decomposed by alkaline solutions. Fly ash is the most common source of alumino-silicate material because the presence of soluble silica and alumina species in fly ash that undergo dissolution, polymerization with the alkali, condensation on particle surfaces, and solidification providing the strength to products. According to the endothermic reaction, heat curing at 40-90 °C for 24-48 h was employed in order to gain high early strength with good physical and mechanical properties. For conventional oven curing, heat is distributed in the specimens from the exterior to the interior leading to the non-uniform and long heat period to attain the require temperature. In contrast, microwave radiation curing, the heat is directly transferred through the specimens and allows faster and more uniform heating due to the interaction between the microwave electric fields and polar molecules. The advantages of this method are removal of water in the fresh cement, collapse of capillary pore, densification of sample and short time curing process.

In this research, we proposed a process using microwave radiation compared to conventional heat curing for the fly ash and aluminium hydroxide waste geopolymer. The results showed that microwave radiation effectively increased the geopolymerization of the geopolymer by reducing the heat curing time. Moreover, the microstructure of geopolymer curing in microwave radiation exhibited more compact than that of conventional oven. It can be supposed that the geopolymer curing in microwave oven leads to the better strength as compared to curing in conventional oven due to the effect of microwave radiation.

#### Polysaccharide Porphyran Extracted from Discolored Laver and its Application to Moisturizing Agent.

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Laver is traditionally consumed in Japan. However, the laver in Japan has recently faced the discoloration problem caused by red tide. Moreover, the discolored laver is more difficult to sell as food because of a bad taste. Consequently, the most of discolored laver is disposed as industrial wastes. Laver consists of Porphyran (POR), sulfate-containing polysaccharide about 15~30wt% that is known to be having various potential biomedical applications especially cosmetic field, due to the pharmacological properties of POR including water holding property, water absorbency, anti- inflammatory effect, and so on. In order to add value to the waste of discolored laver, we focused on the extraction of POR from discolored laver and evaluated the obtained POR properties for using as moisturizing agent. The obtained POR solution were extracted form discolored laver by pressurized heat treatment and subsequently flocculated as POR solid by freeze drying. As a result, yield and color of POR were different due to extraction condition. Moreover, the chemical of POR was identified by measurement with FT-IR and NMR. Molecular weight was determined by GPC. For application to moisturizing agent, we evaluated water retention and allergy inducibility.



Figure.1. Structural formula of Porphyran

#### Green Chemicals Calixarene Hosts Synthesized for Highly Selective Fluorescence Chemo Sensor for Pb<sup>2+</sup>

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Recently, host-guest is well known as selective separator for chemicals. Especially, calixarenes are famous representative molecules synthesized from resorcinol and formyl chemical by compensated reaction as molecule host. We have noted that vanillin (V) and syringaldehyde (S), which are naturally green chemicals, are used to synthesize new calixarene hosts. For example, V and S are harvested from vanilla seed and pine tree as natural chemicals, respectively. These effective uses, therefore, are meaningful in the point of view of sustainable chemistry. In the present study, new V-host and S-host were similarly prepared by dissolving resorcinol, V or S in ethanol for V- or S-host, respectively. The yields of the new hosts of V and S were 32% and 28% respectively. Figure 1 shows chemical structure of V-host. From results of <sup>1</sup>H-NMR and FT-IR, the chemical structure was confirmed successively. Change in UV-VIS absorption and fluorescence spectra of their hosts indicated that the hosting of heavy metal ions such as  $Pb^{2+}$ ,  $Ni^{2+}$ ,  $Cd^{2+}$  and  $Cu^{2+}$  was compared. It was noted in the UV absorption of the phenyl ring of the calixarene was varied, when the inclusion of each heavy metal ion was increased, especially in  $Pb^{2+}$  ion. The observation of the enhanced absorbance intensity was at 280 nm in the UV-VIS spectra. In addition, fluorescence showed that as the calixarenes

coordinated heavy metal ions, especially in  $Pb^{2+}$ , the emission intensity was well quenched. These results were evidenced that the green calixarene was candidate of fluorescent chemo-probe for  $Pb^{2+}$  ion diagnosis.



Figure 1. Chemical structure of V-host

#### Latex-State NMR Spectroscopy for Analysis of Prevulcanization of Isoprene rubber Latex

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Latex-state nuclear magnetic resonance (NMR) spectroscopy is a powerful technique to analyze crosslinking reaction of isoprene rubber, when the rubber is crosslinked in latex stage. For instance, in the previous work, we analyzed vulcanization of natural rubber in latex stage through latex-state <sup>13</sup>C-NMR spectroscopy. Small signals appearing in <sup>13</sup>C-NMR spectrum were carefully assigned to crosslinking junctions of vulcanized natural rubber. This implies that the latex-state NMR spectroscopy open a new field of the in situ analysis of the crosslinked rubbery polymers in latex stage. We may, thus, investigate the mechanism of prevulcanization of isoprene rubber in latex stage through the latex-state NMR spectroscopy.

Figure 1 shows latex-state <sup>13</sup>C-NMR spectra for IR latexes prevulcanized at 50 oC (PVIR50), 70 oC (PVIR70) and 90oC (PVIR90). Signals at 44 ppm were assigned to secondary carbons adjacent to carbons linking to S atoms, whereas signals at 58 ppm were assigned to tertiary and quaternary carbons linking to S atoms. As for PVIR70 and PVIR90 latexes, the signals at 44 and 58 ppm appeared in the latex-state <sup>13</sup>C-NMR spectra. In

contrast, for PVIR50 latex, these signals disappeared in the latex-state <sup>13</sup>C-NMR This implies spectrum. that the prevulcanization of IR latex may occur at temperature above 70 °C. Furthermore, the plausible mechanism of the prevulcanization of isoprene rubber latex suggested to begin with the was abstraction of hydrogen at allylic position of isoprene units.





### P-11

#### **Preparation and Properties of Phenyl-Modified Natural Rubber**

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Phenyl-modified natural rubber, which possesses phenyl groups along with a main chain molecule of *cis*-1,4-polyisoprene, has a potential as a green material. It can be prepared using natural rubber obtained from *Hevea brasiliensis* by directly inserting phenyl groups into the rubber, and may provide a strategic synthesis to control the mechanical properties. One plausible method to insert phenyl groups into NR is Suzuki–Miyaura cross-coupling reaction. For natural rubber, Suzuki–Miyaura cross-coupling reaction. For natural rubber, Suzuki–Miyaura cross-coupling reaction may be processed into two-step. First, a bromine atom is introduced into natural rubber at the allyl position. Second, brominated natural rubber undergoes a cross-coupling reaction with phenyl boronic acid. The second step involves the Suzuki-Miyaura cross-coupling reaction of the brominated natural rubber in the presence of a palladium catalyst. In the present study, we insert phenyl group into NR using the Suzuki-Miyaura cross-coupling reaction.

Figure 1 shows the <sup>1</sup>H-NMR spectra for Brominated natural rubber (BrNR) and the product prepared from BrNR by the Suzuki-miyaura cross-coupling reaction. The large signals at 1.66, 2.03, and 5.12 are attributed to the cis-1,4-isoprene units. After the cross-coupling, several small signals appear around 7.13 ppm, which remain after the acetone extraction, and are assigned to the phenyl groups linked to natural rubber. The signals differ from the signals (7.3 - 7.7 ppm) for phenyl boronic acid. In contrast, the signals at 3.96, 4.15, and 4.44 ppm, which are assigned to allyl bromide groups of Br-NR,

disappear. The signal at 4.92 ppm also disappears. These results demonstrate that the phenyl groups may be linked to natural rubber through the Suzuki-Miyaura cross-coupling reaction. The phenyl groups affected both loss tangent and  $T_g$  of NR.



natural rubber (b) Brominated natural rubber

#### **Crystallization Behavior of Sodium Iron Pyrophosphate Glass**

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Recently, sodium ion second battery is an attractive to be alternative lithium ion second battery because of its natural abundance and low materials costs. So far Honma et al. reported that  $Na_2FeP_2O_7$  glass-ceramics can be used as cathode active materials for sodium ion second battery with high current density rate performance and stable electrochemical cycle performance<sup>[1]</sup>. We focus on the phosphate transition metal glasses that are precursors of  $Na_2FeP_2O_7$ , and we aimed for elucidation of the complicated crystallization mechanism by the valence change of the transition metals and the physical properties evaluation of active materials. In this paper, we fabricated  $Na_2O-FeO-P_2O_5$  glass and investigated physical properties.

The glass composition of Na<sub>2</sub>FeP<sub>2</sub>O<sub>7</sub> precursor glass is 33.3Na<sub>2</sub>O-33.3FeO-

 $33.3P_2O_5 \pmod{33.3NFP}$ . The glass was prepared by a conventional melt-quenching method from NaH<sub>2</sub>PO<sub>4</sub> and FeO. The mixed powder was melted at 900°C for 30min. By pouring melts on iron plate we obtained Na<sub>2</sub>FeP<sub>2</sub>O<sub>7</sub> precursor glass. Differential thermal analysis (DTA) and X-ray diffraction (XRD) analysis were carried out for the melt-quenched samples. To crystallize, quenched glasses heat-treated in N<sub>2</sub> for various times at 430°C or 460°C, and the cross-sections of heat-treated samples observed with scanning electron microscope (SEM).

The cross-sectional SEM image of 33.3NFP heat-treated in  $N_2$  for 4h at 430°C was shown in Fig.1. In Fig.1, the sample was observed surface crystallization tendency with 20-40µm thickness. In addition, inside of the sample was seen the different part of the color and dendritic parts were confirmed. The results were shown that the crystallization mechanism of the glass is complicated.



Fig.1 Cross-sectional SEM image of heat-treated 33.3NFP crystallized glass which obtained by heat-treatment at 430°C for 4h.

 T.Honma et al., Fabrication of Na<sub>2</sub>FeP<sub>2</sub>O<sub>7</sub> glass-ceramics for sodium ion battery, J. Ceram. Soc. Jpn., 120[8] (2012) 344-346

#### Synthesis of Glass-Ceramics Containing High Dialectic Bi<sub>1.5</sub>ZnNb<sub>1.5</sub>O<sub>7</sub> Nanocrystals and Investigation of their Physical Properties.

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Bismuth germanate glasses exhibit high refractive index, wide transparency in the infrared region and good photoluminescence properties. On the other hand,  $Bi_{1.5}$  $ZnNb_{1.5}O_7$  crystal exhibits high permittivity and low-temperature dialectic relaxation.  $Bi_{1.5}$  $ZnNb_{1.5}O_7$  crystals have been synthesized by solid state reaction and sol-gel methods. However, there has been no report about crystallized glasses with  $Bi_{1.5}ZnNb_{1.5}O_7$  crystals. In this study, we focused our attention on the synthesis of transparent crystalized glasses with  $Bi_{1.5}ZnNb_{1.5}O_7$  nanocrystals and investigation of their physical properties.

Glasses with the nominal compositions of  $x(Bi_{1.5}ZnNb_{1.5}O_7)$ -(100-x)GeO<sub>2</sub> (x=50, 60, 65, 70) were prepared by a melt quenching method. Commercial powders of regent grade Bi<sub>2</sub>O<sub>3</sub>, ZnO, Nb<sub>2</sub>O<sub>5</sub>, and GeO<sub>2</sub> were mixed and melted in a platinum crucible at 1100°C for 20 min in an electric furnace. Refractive indices (*n*) at a wavelength of  $\lambda$  = 632.8 nm (He-Ne laser) were measured at room temperature by using a prism coupler. Thermal properties of the glasses were determined by differential thermal analysis (DTA). The glasses were heat-treated and the crystalline phases were identified by X-ray diffraction (XRD). Densities (*d*) of glasses and heat-treated samples were measured by UV-VIS spectrometer and ellipsometer.

The glass of 70(Bi<sub>1.5</sub> ZnNb<sub>1.5</sub>O<sub>7</sub>)-30GeO<sub>2</sub> has the glass transition temperature of  $T_g$ =526°C crystallization temperature of  $T_p$ =619°C and presents the values of *d*=6.33 g/cm<sup>3</sup> and *n*=2.21. The absorption edge of this glass is around 400 nm. The XRD peaks of the heat-treated samples were assigned to the Bi<sub>1.5</sub> ZnNb<sub>1.5</sub>O<sub>7</sub> crystalline phase with a cubic structure. The sample heat-treated at 546°C was transparent and the crystal size estimated by Scherrer equation was ~34 nm, while the sample heat-treated at 560°C was opaque. The other heat-treated samples with x(Bi<sub>1.5</sub>ZnNb<sub>1.5</sub>O<sub>7</sub>)-(100-x)GeO<sub>2</sub> also showed the formation of Bi<sub>1.5</sub> ZnNb<sub>1.5</sub>O<sub>7</sub> crystals. The permittivity and the optical dispersion of the glass and the heat-treated samples will present in the conference.

#### Lanthanide Extraction from Ores

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This work interested in extracting lanthanides from rare earth phosphate minerals called Monazite by focusing on ore digestion and liquid-liquid extraction using di-(ethylhexyl)-phosphoric acid (HDEHP) as extractant. In order to eliminate insoluble phosphates, base-digestion of monazite at 100 °C was performed by studying the effect of NaOH concentration and time. The best digestion was obtained with 70% w/v NaOH for 4 hours. Mineral acid digestion at 80 °C was then carried out in order to dissolve lanthanides into soluble ions. The studied effects of digestion time, acid concentration and acid type showed that the best conditions were attained with 12.1 M (37% v/v) HCl for 2 hours. The results from the study of effects of pH, ligand concentration, contact time, and Na+ concentration in liquid-liquid extraction showed that the optimal condition for HDEHP to extract lanthanide solutions at pH 5 in the presence of 0.01 M Na+ for 5 minutes (66.7 %E). Finally liquid-liquid extraction of real monazite sample solutions collected after nitric acid digestion using ICP-OES quantitative analysis showed percentage extraction of La3+ and Nd3+ to be 21.7% and 17.7%, respectively.

#### **P-15**

#### Fabrication of Pt/TiO<sub>2</sub> Composite Nanofibers by Sol-Gel Reaction combined with Electrospinning Method

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Pt/TiO<sub>2</sub> composite nanofibers (NFs) were prepared by mixing the precusors of titanium isopropoxide (TTIP) and H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O in ethanol and HCl solution and electrospun under the applied voltages in a range of 15-20 kV. This study aimed to investigate the effects of molar ratio of TTIP: ethanol: water: HPt<sub>0.5</sub>Cl<sub>3</sub>, curing temperature and time on the fiber microstructures and to optimize the electrospinning parameters to achieve the uniform Pt/TiO<sub>2</sub> NFs. After calcining at 500°C in air for 3 h, the phase, chemical composition, and microstructures of Pt/TiO2 NFs were then investigated by X-ray diffraction, energy dispersive X-ray spectroscopy, scanning electron microscopy, and transmission electron microscopy techniques, respectively. The results show that the composite nanofibers consisted of uniformly distributed Pt and TiO<sub>2</sub> nanograins, and the phases of anatase, FCC (Pt) and a trace of rutile were observed in the NF structures. The ethanol oxidation activity of the composite NFs was also further investigated and compared with that of commercial Pt/C nanoparticles.

#### Electrical Conductivity of Ca-, Co-Doped PrSr<sub>3</sub>Fe<sub>3</sub>O<sub>10-δ</sub> for IT-SOFCs

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Ruddlesden Popper type oxides of  $LnSr_3Fe_3O_{10-\delta}$  (Ln = La, Pr, Nd, Sm, Eu, and Gd) has recently been introduced as potential cathode for intermediate-temperature solid oxide fuel cells (IT-SOFCs). Its structure as layered perovskites was reported to facilitate the migration of electrons and promotes SOFC performance through oxygen vacancies. In this study,  $PrSr_3Fe_3O_{10-\delta}$  (PSFO10) and its derivatives were prepared by a conventional solid state reaction. The addition of Ca and Co on electrical conductivity of PSFO10 was investigated using a four-probe DC method. The Ca doped materials showed high electrical conductivity compared to the Co doped one. The electrical conductivity of Ca doped PSFO10 varied depending on the A site substitution. The Ca substitution at Sr site had more affect than those at the Pr site.

#### Controlling Color Transition of Polydiacetylene/Zinc Oxide Nanocomposites Dispersed in Toluene by Varying Alkyl Chain Length of Cationic Surfactant

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Polydiacetylene (PDA) exhibit colorimetric response to several external stimuli; therefore, it has received attentions for sensing technology. Our research group incorporates zinc oxide (ZnO) nanoparticles into the PDA vesicle to improve the properties of PDA-based materials and PDA/ZnO nanocomposite is successfully fabricated. The PDA/ZnO nanocomposite exhibits higher color transition temperature than the pure PDAs, and also reversible thermochromism [1,2]. In addition, the PDA/ZnO nanocomposite can be dispersed in various organic solvents provide that can be mixed with various polymer matrices for solid-state fabrication. We also observe that utilization of polymeric dispersants improves dispersion stability and film homogeneity [3]. In this ongoing research, cationic surfactants including cetyltrimethylammonium bromide (CTAB), dodecyltrimethylammonium bromide (DTAB), and decyltrimethylammonium bromide are used in the system of PDA/ZnO nanocomposite dispersed in toluene. Differences in alkyl chain length of these cationic surfactants are expected to alter suspension stability and thermochromic behaviors of the nanocomposite. It is found that increasing in alkyl chain length of cationic surfactant tends to decrease color-transition temperature and color reversibility of the nanocomposite. Effects of surfactant concentration on dispersion stability and color-transition of PDA/ZnO nanocomposite are also investigated.

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**P-17** 

#### **Biotransformation of Solar Energy and CO<sub>2</sub> into Bioplastic Polyhydroxybutyrate (PHB) by Photosynthetic Cyanobacteria**

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PHB is a biopolymer exhibiting thermostability and hardness comparable to those petroleum-based plastic; however, PHB content is known in a limited number of cyanobacteria. This study examined PHB contents in 137 cyanobacterial strains (29 genera, 88 species) under photosynthetic condition using atmospheric CO<sub>2</sub> as carbon source. Cellular PHB accumulations were low in all strains under the normal culture condition. Nitrogen-deficient condition significantly raised PHB accumulation in 63 strains, the greater frequency than acquired by potassium, phosphorus, or all-nutrient deprivation. High levels of PHB accumulation did not associated to certain evolutionary linkage, but was strain specific. *Calothrix* sp. that its filament biomass, harvested by filtration at 92.4 ± 66.6 % (w/w), produced PHB at 356.5 ± 63.4 mg/L (accounting for biomass of 1396.6 ± 66.1 mg/L and PHB content of 25.4 ± 3.5% w/w DW). This PHB production is equivalent to the CO<sub>2</sub> utilization of 0.73 ± 0.13 g/L. The obtained cyanobacterial PHB has comparable material properties to those of commercial PHB. Through culture optimization, the maximal energy conversion from light to PHB proceeded by this cyanobacterium was  $1.42 \pm 0.30\%$ .

Keywords: cyanobacteria; bioplastic; PHB, CO<sub>2</sub>, energy

#### Biodegradation Kinetics of Organophosphate Insecticide by Pseudomonas Plecoglossicida PF1

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*Pseudomonas plecoglossicida* PF1 (referred to as PF1) was isolated from agricultural soil with pesticide use as an organophosphate-degrading bacterium. Its ability to degrade organophosphate insecticide was focused to profenofos, which is one of the heavily used pesticides in crop areas in Thailand. Profenofos has relatively high water solubility; therefore it is contaminated not only in surface water, but also in groundwater where oxygen level is limited. As a result, this study investigated profenofos biodegradation by PF1 aerobically and anoxically with nitrate supplement. The biodegradation kinetic was conducted with various concentrations of profenofos under both conditions having the removal efficiency of 38-55% and 27-45%, respectively. During the degradation, the increase of cell growth from  $10^4$  to  $10^8$  CFU/ml confirmed that profenofos was utilized for cell biomass. This results indicated that *Pseudomonas plecoglossicida* PF1 has potential to be applied as bioaugmented culture for bioremediation in the profenofos-contaminated environment including groundwater containing nitrate.

*Keywords*: Profenofos biodegradation, Pseudomonas plecoglossicida, Nitrate, Aerobic, Anoxic

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