

# MANA

## International Symposium 2009

### Jointly with ICYS

2009  
**2/25 (WED) - 27 (FRI)**

Venue: Epochal Tsukuba, Japan

Details: [http://www.nims.go.jp/mana\\_2009/](http://www.nims.go.jp/mana_2009/)



World Premier International (WPI) Research Center  
International Center for  
Materials Nanoarchitectonics (MANA), NIMS



National Institute for Materials Science (NIMS)



## Welcome address



**Teruo Kishi**  
Chief Project Officer, MANA  
President, NIMS

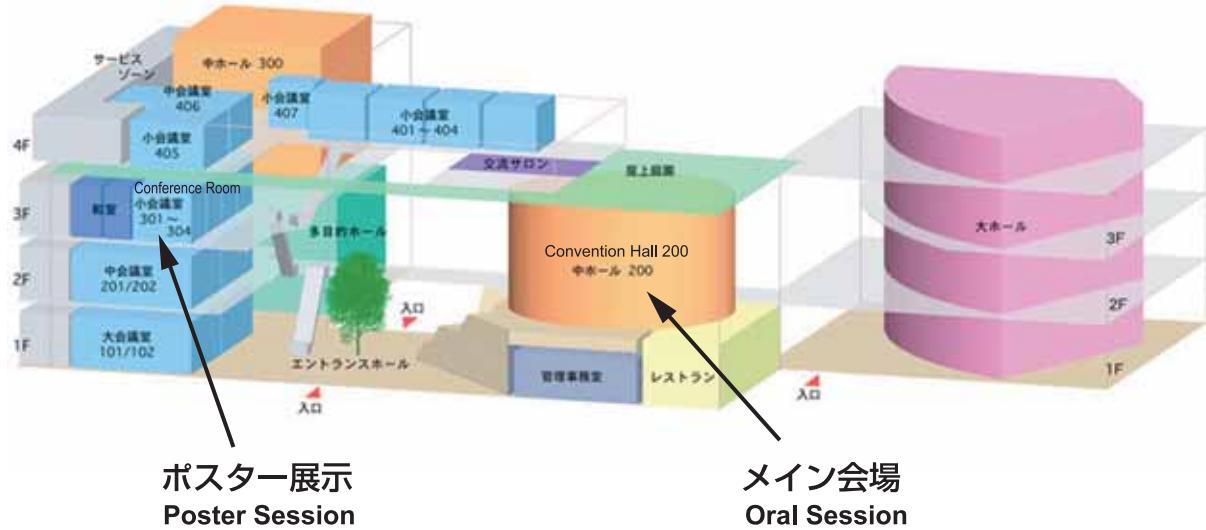
After the inauguration of MANA in October 2007, we have continued to search for the best structure of the organization of MANA as a world premier international research center supported by MEXT. As a result, one year after the inauguration, in October 2008, MANA was restructured as follows. The previous grouping into five research fields based on the key technologies was changed to a new grouping into four research fields: 1) Nano-Materials, 2) Nano-System, 3) Nano-Green, and 4) Nano-Bio. At the 2<sup>nd</sup> MANA International Symposium, we would like to present the research directions of these four fields.

The unchanged goal of MANA is based on our conviction that materials are the mother of science and technology. We therefore believe that many of future technologies necessary for the sustainable development of our society in the 21<sup>st</sup> century cannot be realized without the development of novel materials. To meet the demand, MANA is attempting to open a new paradigm of materials development based on a new technology system named “materials nanoarchitectonics”, where nanoscale structural units are arranged in a desired configuration to create new functionality by manipulating the interaction between the units. This challenge is tackled with the innovative development and integration of five key technologies: a) novel atom and molecule manipulation, b) controlled self-organization, c) chemical nanostructure manipulation, d) field-induced materials control, and e) theoretical modeling and designing. By advancing research in this new realm, MANA will open a new paradigm of materials development that can assure significant contributions to our society in such forms as environmental and energy sustainability, next-generation computation and communication, and regenerative medicine.

At this 2<sup>nd</sup> MANA International Symposium, presentations are made by a wide variety of speakers, i.e. distinguished scientists as invited speakers and a special lecturer, several MANA Principal Investigators, MANA Scientists, and young MANA Independent Scientists. We hope all participants to this symposium will obtain fresh inspiration from the presentations and mutual discussions.

MANA International Symposium 2009  
February 25th to 27th, 2009

February 24 (Tue)	February 25 (Wed)	February 26 (Thu)	February 27 (Fri)
	Registration	Registration	Registration
	Opening Remark		
	Greeting		
	Introduction of the WPI Program	Nano-Materials 3	ICYS 1
	Outline of MANA		
	Special Lecture	Coffee Break	Coffee Break
	Coffee Break		
	Nano-Materials 1	Nano-System 1	ICYS 2
	Lunch	Lunch	Lunch
	Nano-Materials 2	Nano-System 2	Nano-Green
	Coffee Break	Coffee Break	Coffee Break
	Nano-Bio	Brief Presentations of Posters	Nano-Green
			Closing Remark
		Poster Sessions	
Registration			
Reception		Banquet	





**PROGRAM**  
**MANA International Symposium 2009**  
**25<sup>th</sup> - 27<sup>th</sup> February, 2009**

**Venue: Tsukuba International Congress Center EPOCHAL TSUKUBA**  
**(Address: 2-20-3, Takezono, Tsukuba, Ibaraki, 305-0032, Japan)**

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**February 25<sup>th</sup>**

**Opening**

*(Chair: Yoshio Bando)*

9:30 - 9:40     *Opening Address*  
                  **Teruo Kishi** (Chief Project Officer of MANA; President of NIMS)

9:40 - 9:45     *Greetings*  
                  **Hiroo Imura** (Chairperson of the Program Committee of the WPI Initiative;  
                  Professor Emeritus of Kyoto University)

9:45 - 10:05     *Introduction of the WPI Program*  
                  **Toshio Kuroki** (Program Director of WPI Program;  
                  Deputy Director of Research Center for Science Systems, JSPS)

10:05 - 10:20     *Outline of MANA*  
                  **Masakazu Aono** (Director-general of MANA, NIMS)

10:20 - 10:50     *Special Lecture: Grand Challenges in Nano Science & Technology*  
                  **Heinrich Rohrer** (Nobel Laureate in Physics 1986)

10:50 - 11:10     *Coffee Break & Group Photograph at the Main Entrance*

**Nano-Materials 1**

*(Chair: Zhong-Lin Wang, Katsuhiko Ariga)*

11:10 - 11:40     *Molecular Architectures from Cyclodextrins for Biomedical Applications (Invited)*  
                  **Gerhard Wenz** (Professor, Saarland University)

11:40 - 12:00     *Biotemplated Nanofabrication and Bioinspired Nanotechnology*  
                  **Zhong-Lin Wang** (MANA Satellite Principal Investigator;  
                  Professor, Georgia Institute of Technology)

12:00 - 12:15     *Molecular Beyonds*  
                  **Kentaro Tashiro** (MANA Scientist, NIMS)

12:15 - 13:30     *Lunch*

**Nano-Materials 2**

(Chair: *Takayoshi Sasaki & Masayoshi Higuchi*)

13:30 - 13:50 *Toward Higher Performance Permanent Magnets for Automotive Applications*  
**Kazuhiro Hono** (MANA Principal Investigator, NIMS)

13:50 - 14:10 *Electromechanical Properties and Engineering of Nanotubes, Nanowires, Nanobelts and Nanocones in a Transmission Electron Microscope*  
**Dmitri Golberg** (MANA Principal Investigator, NIMS)

14:10 - 14:25 *Oxide Nanosheets: New Solution to Nanoelectronics*  
**Minoru Osada** (MANA Scientist, NIMS)

14:25 - 14:40 *Novel Electrochromic Materials and Their Solid-state Devices*  
**Masayoshi Higuchi** (MANA Independent Scientist, NIMS)

14:40 - 15:00 *Coffee Break*

**Nano-Bio**

(Chair: *Yuji Miyahara & Jun Nakanishi*)

15:00 - 15:30 *Intelligent Nanostructured Surface for Cell Sheet Tissue Engineering (Invited)*  
**Teruo Okano** (Professor, Tokyo Women's Medical University)

15:30 - 15:50 *Detection of biomolecular recognition using bio-transistors*  
**Yuji Miyahara** (MANA Principal Investigator, NIMS)

15:50 - 16:05 *Bio compatibility Evaluation of Bioabsorbable Magnesium Alloys*  
**Akiko Yamamoto** (MANA Scientist, NIMS)

16:05 - 16:10 *Break*

16:10 - 16:30 *Nano-particle Assisted Therapy*  
**Yukio Nagasaki** (MANA Satellite Principal Investigator; Professor, Tsukuba University)

16:30 - 16:45 *Manipulation of Stem Cell Functions by Patterned Polymer Surfaces*  
**Guoping Chen** (MANA Scientist, NIMS)

16:45 - 17:00 *Novel Biointerface with Well-Defined, Concentrated Polymer Brushes Obtainable by Surface-Initiated Living Radical Polymerization.*  
**Chiaki Yoshikawa** (MANA Independent Scientist, NIMS)

17:00 - 17:15 *Photoresponsive Biointerfaces for Cell Analysis*  
**Jun Nakanishi** (MANA Independent Scientist, NIMS)

**February 26<sup>th</sup>**

**Nano-Materials 3**

(Chair: *Eiji Takayama-Muromachi*)

9:15 - 9:45 *Recent Developments in Hybrid Inorganic-Organic Framework Materials* (Invited)  
**Anthony Cheetham** (Professor, University of Cambridge)

9:45 - 10:15 *Control of Composition, Structure, and Morphology of Mesostructured Materials*  
**Kazuyuki Kuroda** (Professor, Waseda University) (Invited)

10:15 -10:35 *Coffee Break*

**Nano-System 1**

(Chair: *Masakazu Aono & Roland Wiesendanger*)

10:35 - 11:05 *Atomic-scale Structure and Dynamics of Magnetic Nano-systems* (Invited)  
**Roland Wiesendanger** (Professor, University of Hamburg)

11:05 - 11:25 *MANA-CNSI Overview*  
**James Gimzewski** (MANA Satellite Co-Director & MANA Satellite Principal Investigator; Professor, UCLA)

11:25 - 11:45 *Nano Superconductivity as a Novel Source of THz Electromagnetic Wave*  
**Xiao Hu** (MANA Principal Investigator, NIMS)

11:45 - 12:00 *Nanoscale Electrical Transport Measurement by Multiple-scanning-probe Microscopes*  
**Osamu Kubo** (MANA Scientist, NIMS)

12:00 - 12:15 *Synthesis and Impurity Doping in Germanium Nanowires as the Basis for Next- generation Semiconductor devices*  
**Naoki Fukata** (MANA Independent Scientist, NIMS)

12:15 -13:30 *Lunch*

**Nano-System 2**

(Chair: *James K. Gimzewski & Hideaki Takayanagi*)

13:30 - 14:00 *Electric-field-induced Superconductivity in an Insulator* (Invited)  
**Masashi Kawasaki** (Professor, Tohoku University)

14:00 - 14:20 *Spin-polarized CarrierInjection Effect in a Ferromagnetic Semiconductor/Diffusive Semiconductor/Superconductor*  
**Hideaki Takayanagi** (MANA Satellite Principal Investigator; Professor, Tokyo University of Science)

14:20 - 14:40 *Atomic Switch for Neural Networking Systems*  
**Tsuyoshi Hasegawa** (MANA Principal Investigator, NIMS)

14:40 - 14:55 *Connection of Molecular Nanowires to Single Functional Molecules*  
**Yuji Okawa** (MANA Scientist, NIMS)

14:55 -15:15 *Coffee Break*

15:15 -16:40 **Brief Presentations for posters** (Chair: *Tsuyoshi Hasegawa*)

16:45 -18:30 **Poster Session**

19:00 -21:00 *Banquet*

February 27<sup>th</sup>

## ICYS 1

(Chair: Sukekatsu Ushioda &amp; Daisuke Fujita)

9:30 - 9:45 *Engineering the Properties of Heusler Alloys for Spintronic Devices.*  
**Rajanikanth Ammanabrolu** (ICYS Researcher, NIMS)

9:45 - 10:00 *Chemical Order in Ternary Complex Metallic Alloys*  
**Cezar Gomez** (ICYS-MANA Researcher, NIMS)

10:00 - 10:15 *Nano Structured Materials Design with Phase Separation*  
**Byung-Joo Park** (ICYS Researcher, NIMS)

10:15 - 10:30 *Templated Synthesis of Electrically Conductive Organic Materials*  
**Yasuhiro Shirai** (ICYS-MANA Researcher, NIMS)

10:30 - 10:50 *Coffee Break*

## ICYS 2

(Chair: Shunichi Hishita &amp; Koichi Tsuchiya)

10:50 - 11:05 *Nanopatterning Self-assembling Polymers*  
**Michael Lee** (ICYS-MANA Researcher, NIMS)

11:05 - 11:20 *Development of High Field Superconducting Magnets*  
**David Uglietti** (ICYS Researcher, NIMS)

11:20 - 11:35 *Three-dimensional Imaging with Confocal Scanning Transmission Electron Microscopy*  
**Ayako Hashimoto** (ICYS Researcher, NIMS)

11:35 - 11:50 *Ab initio Molecular Dynamics: an Atomic-scale Simulation Approach to Nanoscience and Nanotechnology*  
**Roberto Scipioni** (ICYS-MANA Researcher, NIMS)

11:50 - 13:30 *Lunch*

## Nano-Green 1

(Chair: Enrico Traversa &amp; Yoshitaka Tateyama)

13:30 - 14:00 *Drastic Current Increase in Microbial Fuel Cell by the Addition of  $Fe_2O_3$*  (Invited)  
**Kazuhito Hashimoto** (Professor, University of Tokyo)

14:00 - 14:30 *Toward First-principles Electrochemistry* (Invited)  
**Nicola Marzari** (Professor, Massachusetts Institute of Technology )

14:30 - 14:50 *Atomic and Molecular Assemblies for Efficient Energy Conversion at Solid/Liquid Interfaces*  
**Kohei Uosaki** (MANA Satellite Principal Investigator; Professor, Hokkaido University)

14:50 - 15:05 *Ab Initio MD Study on Redox Reactions in Electrolyte Solutions of DSSC*  
**Yoshitaka Tateyama** (MANA Independent Scientist, NIMS)

15:05 - 15:25 *Coffee Break*

**Nano-Green 2**

(Chair: Kohei Uosaki & Yusuke Yamauchi)

15:25 - 15:45 *Design of Catalytically Active Site for Catalytic Conversion of Biomass*

**Keiichi Tomishige** (MANA Satellite Principal Investigator;  
Associate Professor, University of Tsukuba)

15:45 - 16:05 *Highly Efficient Dye-sensitized Solar Cells*

**Liyuan Han** (MANA Principal Investigator, NIMS)

16:05 - 16:25 *Tailoring Nanostructured Oxide Thin Films for the Miniaturization of Solid Oxide Fuel Cells*

**Enrico Traversa** (MANA Principal Investigator, NIMS)

16:25 - 16:40 *Design of Nanoarchitected Electrodes for Next-generation Batteries*

**Yusuke Yamauchi** (MANA Independent Scientist, NIMS)

16:40 - 16:45 *Closing Remarks*

**Yoshio Bando** (MANA Chief Operating Officer, NIMS)

**Poster Session**  
**26<sup>th</sup> February, 2009**

**Nano-Materials**

**PM-1** *Towards thermo-conductive electrically insulating polymeric composites using BN nanotubes as fillers*  
**Yoshio Bando** NIMS, JAPAN

**PM-2** *Novel Concept for Formation of Boron Nitride Nanoparticles*  
**Chengchun Tang** NIMS, JAPAN

**PM-3** *Compositional design, structural analysis and property studies of one-dimensional (1D) wide band-gap semiconductor nanostructures*  
**Baodan Liu** NIMS, JAPAN

**PM-4** *Multifunctional Boron Network Compounds as Novel Energy Materials*  
**Takao Mori** NIMS, JAPAN

**PM-5** *Preparation and photoluminescence characterizations of Ln-photoactivated oxide nanosheets for new phosphor development*  
**Tadashi Ozawa** NIMS, JAPAN

**PM-6** *A Topochemical Approach to Transition-metal Layered Double Hydroxide (LDH) Nanosheets*  
**Renzhi Ma** NIMS, JAPAN

**PM-7** *Microwave-Polyol Synthesis of Size-Controlled ZnO Colloidal Nanocrystal Clusters*  
**Xianluo Hu** JSPS Fellow, NIMS, JAPAN

**PM-8** *Fabrication of Selectivity Controllable Gas Sensor Film Composed by Hollow Mesoporous Carbon Capsules*  
**Qingmin Ji** NIMS, JAPAN

**PM-9** *Supermolecular Complexes of Oligochromophores with substituted Fullerene*  
**Jonathan Hill** NIMS, JAPAN

**PM-10** *Morphological Aspects of Phase Separation in Poly(Vinyl Methyl Ether) /Water/Ethanol Solutions*  
**Jan Labuta** JSPS Fellow, NIMS, JAPAN

**PM-11** *A Convenient Preparation Method for Polymer/Carbon Nanotube Composites with A Core/Shell Structure by In Situ Polymerization Induced by UV Irradiation*  
**Xiao-Yan Yu** NIMS, JAPAN

**PM-12** *Hierarchical self-assembly of OPV at the air-water interface*  
**Chithra Parayalil** NIMS, JAPAN

**PM-13** *Fabrication of gold nanotape architecture using in-situ generated 1D template*  
**Saikat Mandal** JSPS Fellow, NIMS, JAPAN

**PM-14** *Fluorescence response upon volatile organic solvents to oligo-phenylene phenols*  
**Ken Okamoto** NIMS, JAPAN

**PM-15** *Towards N-Type Acene Derivatives for Organic Electronic Applications*  
**Gary James Richards** NIMS, JAPAN

**PM-16** *Charged Molecules Manipulation Using Nano-Domain Patterned Ferroelectric Templates*  
**Kenji Kitamura** NIMS, JAPAN

**PM-17** *Polymer Blends for Nano-structured Photovoltaic Effect*  
**Fumio Ohuchi** University of Washington, U.S.A.

**PM-18** *Post-perovskite transition of the correlated 4d oxide  $CaRhO_3$*   
**Kazunari Yamaura** NIMS, JAPAN

**PM-19** *Superconducting properties of the oxygen-vacant iron oxyarsenide  $TbFeAsO_{1.8}$*   
**Youguo Shi** NIMS, JAPAN

**PM-20** *Formation of crystalline-oriented titania thin films on ITO glass electrodes by electrophoretic deposition in a strong magnetic field*  
**Mamiko Kawakita** NIMS, JAPAN

**PM-21** *Correlation between applied pressure, homogeneity, properties and microstructure in pure ultrafine WC powder consolidated by Spark Plasma Sintering (SPS)*  
**Salvatore Grasso** NIMS, JAPAN

**PM-22** *A Surface Chemistry Leading to the Unique Optical Properties from Silicon Nanoparticles*  
**Naoto Shirahata** NIMS, JAPAN

**PM-23** *Improvements on sintering by optimizing the colloidal processing*  
**Suarez Gustavo** NIMS, JAPAN

**PM-24** *Electric Properties of Nano-structured Metal Oxides I*  
**Naoki Ohashi** NIMS, JAPAN

**PM-25** *Electric Properties of Nano-structured Metal Oxides II*  
**Jian-Yong Li** NIMS, JAPAN

**PM-26** *Optically monitored wet chemical preparation of plasmonic nanostructures for surface enhanced IR absorption spectroscopy*  
**Dominik Enders** NIMS, JAPAN

**PM-27** *Stepwise metal assembling dendrimers and the application to organic electronics devices and atom technology for novel metal oxide materials*  
**Norifusa Satoh** Keio University, JAPAN

**PM-28** *Synthesis and Characterization of NIR-Emitting Semiconductor Nanocrystals*  
**Saim Emin** Saitama University, JAPAN

### Nano-System

**PS-1** *Fabrication and characterization of individual  $ZnO$  nanowires*  
**Makoto Sakurai** NIMS, JAPAN

**PS-2** *Preparation of cell specimens for nanometrology*  
**Hiromi Kuramochi** NIMS, JAPAN

**PS-3** *Conductive-area-controlled carbon nanotube probes for biological applications*  
**Hiroyuki Tomimoto** NIMS, JAPAN

**PS-4** *Single molecule SERS with tungsten oxide nanorod*  
**Yoshitaka Shingaya** NIMS, JAPAN

**PS-5** *MIS-Diode-Typed Reaction Stages for Nano-Bio Interfaces –Detection of Antigen-Antibody Interactions for Tumor Markers*  
**Makoto Sawamura** NIMS, JAPAN

**PS-6** *Development of multiple-scanning-probe force microscope*  
**Seiji Higuchi** NIMS, JAPAN

**PS-7** *Reversibility-controlled chemical reaction between fullerene molecules and its application for information storage devices*  
**Masato Nakaya** NIMS, JAPAN

**PS-8** *Study of the switching mechanism for  $Ta_2O_5$ -based solid electrolyte resistive switch*  
**Tohru Tsuruoka** NIMS, JAPAN

**PS-9** *Synthesis and characterization of ionic conductor nanowires for unique nanoionics devices*  
**Kazuya Terabe** NIMS, JAPAN

**PS-10** *Radiation of Terahertz Electromagnetic Wave from High- $T_c$  Superconductors*  
**Shizeng Lin** NIMS, JAPAN

**PS-11** *Quasiparticles in anisotropic triangular antiferromagnets*  
**Masanori Kohno** NIMS, JAPAN

**PS-12** *Fabrication and characterization of noble metal nanoparticle structures on the surface of highly ordered pyrolytic graphite wafer*  
**Xinli Guo** NIMS, JAPAN

**PS-13** *Surface compositions and structures on  $\alpha$ -phase Cu-9 at. % Al(111) alloy*  
**Yinghui Yu** NIMS, JAPAN

**PS-14** *Auger Electron Spectroscopy and Surface Potential of Few Layer Graphene Films Grown on Polycrystalline Metal Surfaces*  
**Jianhua Gao** NIMS, JAPAN

**PS-15** *Silicon nanoparticles as fluorescent labeling of living cells*  
**Keisuke Sato** NIMS, JAPAN

**PS-16** *Selective molecular assembly for solution-based fabrication of organic field-effect transistors*  
**Kazuhito Tsukagoshi** NIMS, JAPAN

**PS-17** *Superconductivity and Magnetic Ordering Induced by Yttrium-doping in  $AFe_2As_2$  ( $A = Sr, Ca$ )*  
**Shen V. CHONG** University of Tsukuba, JAPAN

**PS-18** *Several microwatt level of emission from rectangular shape Bi2212 mesa  
-improvement in radiation power and towards the realization of THz generator-*  
**Kazuhiro Yamaki** University of Tsukuba, JAPAN

**PS-19** *Terahertz Radiation from Cylindrical Structure of Intrinsic Josephson Junction System of  $Bi_2Sr_2CaCu_2O_{8+\delta}$*   
**Manabu Tsujimoto** University of Tsukuba, JAPAN

**PS-20** *Probing Nanocapsules for Targeted Drug Delivery by Atomic Force Microscopy*  
**Adam Z. Stieg** UCLA, USA

### Nano-Green

**PG-1** *Preparation of Nitrogen-Doped Lamellar Solid Acids with Visible Light-Responsive Photocatalytic Activities*  
**Xiukai Li** NIMS, JAPAN

**PG-2** *Semiconductor Nanoparticle Assemblies: Adjustable Band Gap and Photocatalytic Applications*  
**Tong Hua** NIMS, JAPAN

**PG-3** *Interfacial molecular structure at solid/liquid interfaces by surface sensitive vibrational spectroscopies.*  
**Hidegoro Noguchi** Hokkaido University, JAPAN

**PG-4** *Single Molecule Manipulation in a Lipid Bilayer using Metal Nanogates*  
**Kei Murakoshi** Hokkaido University, JAPAN

**PG-5** *Chemosselective hydrogenolysis of tetrahydrofurfuryl alcohol to 1,5-pentanediol*  
**Shuichi Koso** University of Tsukuba, JAPAN

**PG-6** *Development of catalytic process of  $CO_2$  conversion to organic carbonate*  
**Masayoshi Honda** University of Tsukuba, JAPAN

**Nano-Bio**

**PB-1** *Detection of Supported Lipid Bilayers Using Their Electric Charge*  
**Chiho Kataoka** NIMS, JAPAN

**PB-2** *Improved anti-thrombogenic and endothelial cell adhesive properties of citric acid-crosslinked collagen*  
**Tetsushi Taguchi** NIMS, JAPAN

**PB-3** *Electrospray Deposition as a New Method for Preparing Fine Drug Particles*  
**Kohsaku Kawakami** NIMS, JAPAN

**PB-4** *Live cell-based sensor devices*  
**Akiyoshi Taniguchi** NIMS, JAPAN

**PB-5** *Building a novel transcriptional regulator as a universal switch platform*  
**Tomohiko Yamazaki** NIMS, JAPAN

**PB-6** *Bioreactivity of PEGylated gold surfaces constructed by mixed homo-/hetero-telechelic PEGs*  
**Keitaro Yoshimoto** University of Tsukuba, JAPAN

**PB-7** *Evaluation of nanomaterials based on molecular biology*  
**Junko Okuda** NIMS, JAPAN

**PB-8** *Construction of a antiferritin/mixed-PEG coimmobilized soft surface onto polystyrene nanospheres to improve its immunodiagnosis performance*  
**Xiaofei Yuan** University of Tsukuba, JAPAN

**PB-9** *Cytoplasmic Delivery of siRNA Based on the Polyion Complex with Cross-Linked Polyamine Nanogels Directed to Enhance the Gene Silencing Efficiency*  
**Atsushi Tamura** University of Tsukuba, JAPAN

**PB-10** *PEG-polyamine/DNA co-immobilized gold surfaces as a novel platform for DNA sensing: Comparison of PEG-b-polyamine layer and polyamine-g-PEG layer using XPS analysis*  
**Shinya Matsumoto** University of Tsukuba, JAPAN

**PB-11** *Modulation of lysozyme activity by smart copolymer PEAMA-g-PEG: Recovery of its enzymatic activity after heat treatment using polyion complex chemistry*  
**Ganguli Sumon** University of Tsukuba, JAPAN

**PB-12** *Luminescence-based Colorimetric Discrimination of Single-nucleotide Transversions by the Combined Use of the Derivatives of DOTA-conjugated Naphthyridine and Its Terbium Complex*  
**Hiroshi Atsumi** University of Tsukuba, JAPAN

**PB-13** *Effects of Mixed-Poly(ethylene glycol) Tethered Chain Layer on Activity of Fab' Fragment on a Gold Sensor Surface*  
**Motohiko Nishio** University of Tsukuba, JAPAN

**PB-14** *Cross-linked Polymer Micelles with Biodegradable Ionic Cores for Drug Delivery*  
**Tatiana K. Bronich** University of Nebraska Medical Center, U.S.A.

**MANA Independent Scientist**

**PIS-1** *Atom-scale and Mesoscale Infrared Plasmonic Metrials*  
**Tadaaki Nagao** NIMS, JAPAN

**PIS-2** *Effects of cation and oxygen doping on structural, physical, and chemical properties of multiferroic  $BiMnO_3$  and  $BiCrO_3$*   
**Alexei Belik** NIMS, JAPAN

**PIS-3** *Highly Crystalline and Active Nanoporous Metallosilicate Nanocages*  
**Ajayan Vinu** NIMS, JAPAN

**PIS-4** *Superconductivity of FeSe and related compounds*  
**Shunsuke Tsuda** NIMS, JAPAN

**PIS-5** *A graphene-based double quantum-dot system*  
**Satoshi Moriyama** NIMS, JAPAN

### ICYS Researcher

**PIR-1** *Solution Synthesis, Cathodoluminescence, and Field-Emission Properties N-Doped ZnO Nanobullets*  
**Ujal Gautam** NIMS, JAPAN

**PIR-2** *One-Dimensional (1D) Semiconductor ZnS Nanostructures -- Novel Functional Materials*  
**Xiaosheng Fang** NIMS, JAPAN

**PIR-3** *A versatile application of electron-beam-induced current technique in semiconductor diagnosis*  
**Jun Chen** NIMS, JAPAN

**PIR-4** *Fabrication of oriented oxide films by pulsed laser deposition using two-dimensional inorganic nanosheet as a seed layer*  
**Tatsuo Shibata** NIMS, JAPAN

**PIR-5** *Development of Ordered Nanoporous Materials for Electrochemical Applications*  
**Pavuluri Srinivasu** NIMS, JAPAN

**PIR-6** *Phase modulation of quasi-one-dimensional charge-density waves induced by impurities*  
**Canhua Liu** NIMS, JAPAN

**PIR-7** *Deep-ultraviolet Diamond-based Photodetector for high-power excimer lamp*  
**Masataka Imura** NIMS, JAPAN

**PIR-8** *An Efficient Route to Rattle-type  $Fe_3O_4@SiO_2$  Hollow Mesoporous Spheres Using Colloidal Carbon Spheres Templates*  
**Yufang Zhu** NIMS, JAPAN

**PIR-9** *ZnO nanostructures-mediated cell viability*  
**Mingsheng Xu** NIMS, JAPAN

**PIR-10** *Ruthenium complexes for artificial endonucleases: DFT analysis of ligands and potential binding interactions with DNA*  
**Antonio Sanchez Torralba** NIMS, JAPAN

**PIR-11** *Effect of liquid superheating on liquid supercooling of Al particles*  
**Qingsong Mei** NIMS, JAPAN

**PIR-12** *Facile Synthesis of Ultralong Cadmium Chalcogenide Nanotubes by Sacrificial Template Route from 1D Cadmium Hydroxide Nanowires Bundles*  
**Vaishali Shinde** NIMS, JAPAN



# MANA

## International Symposium

# 2009

**Greetings**



**Name (Title):** Hiroo Imura (Chairperson of the Program Committee of the WPI Initiative, Professor Emeritus of Kyoto University, Chief Fellow of CRDS)



**Affiliation:**

Center for Research and Development Strategy(CRDS)  
Japan Science and Technology Agency(JST)

**Address:**

Kojimachi Square Buiding 3F,  
3, Nibancho, Chiyoda-ku, Tokyo 102-0084 Japan

**Presentation Title:**

Greetings

**Name (Title):** Toshio Kuroki ( Program Director of WPI Program;  
Deputy Director of Research Center for Science Systems )



**Affiliation:**

Japan Society for the Promotion of Science (JSPS)

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8, Ichibancho, Chiyoda-ku, Tokyo, 102-8472 JAPAN

**Email:** tkuroki@jps.go.jp

**Home Page:** <http://www.jps.go.jp>

**Presentation Title:**

Introduction of the WPI Program

**Name (Title):** Masakazu Aono ( Director General of MANA )



**Affiliation:**

National Institute for Materials Science (NIMS)

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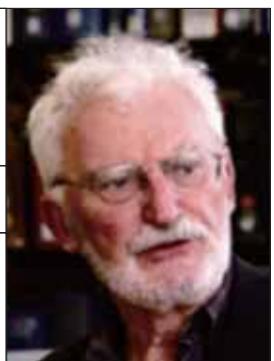
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**Presentation Title:**

Outline of MANA

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**Presentation Title:**  
Special Lecture: Grand Challenges in Nano Science & Technology



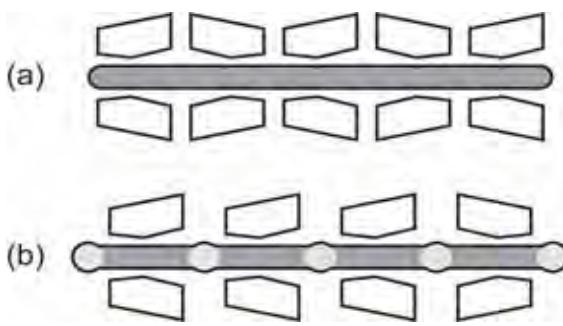
# MANA

## International Symposium

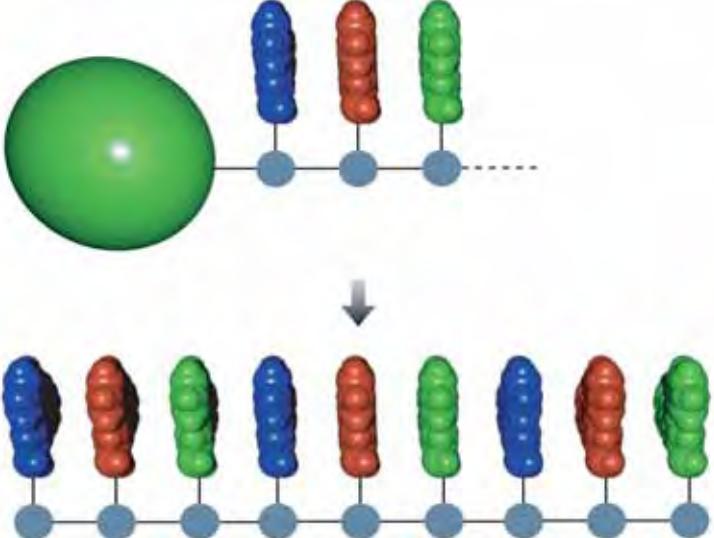
# 2009

**Oral Presentation**

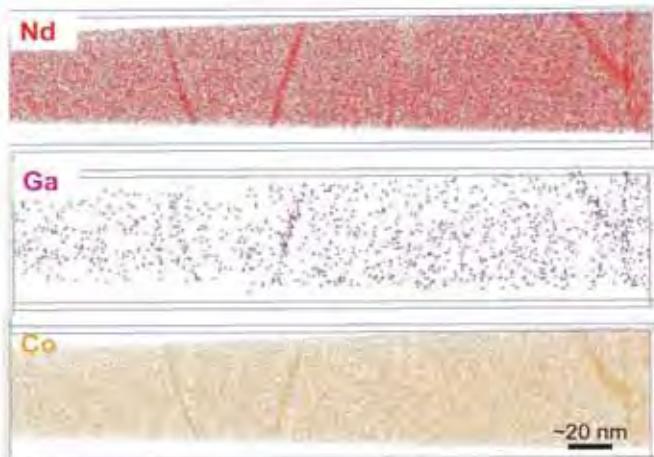


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<b>Presentation Title:</b> Molecular Architectures from Cyclodextrins for Biomedical Applications	
<p><b>Abstract:</b>            Cyclodextrins are doughnut-shaped cyclic oligomers of amylose consisting of 6, 7 or 8 glucose units called <math>\alpha</math>-, <math>\beta</math>- or <math>\gamma</math>-CDs, respectively. Cyclodextrins are able to complex both monomeric and polymeric guest molecules in aqueous solution.<sup>[1]</sup> Cyclodextrins spontaneously thread onto many linear polymers, such as polyethers,<sup>[2]</sup> polyesters or polysiloxanes in aqueous media due to hydrophobic interactions.<sup>[3]</sup> The resulting pseudo-polyrotaxanes are generally insoluble in water, since the CD rings are tightly packed linearly along the polymer chain forming so-called channel inclusion compounds (s. Scheme 1 a).            On the other hand, highly water-soluble ionic polymers with sufficiently long hydrophobic spacer groups, so-called poly(bola-amphiphiles) allow threading under homogenous conditions in aqueous solution.<sup>[4]</sup> CD rings are separated by the ionic groups which also control the rates of threading and dissociation (s. Scheme 1b).<sup>[5]</sup> </p>	
	
<p>Scheme 1. Complexes of (a) hydrophobic, (b) bola-amphiphilic polymers and cyclodextrins</p>	
<p>Pseudopolyrotaxanes can be used as supramolecular entities showing a programmable lifetime, which should be very useful for bio-medical applications. Polyfunctional pseudopolyrotaxanes equipped with specific ligands, such as sugars, might be applicable for the targeted delivery of drugs. Cationic polyrotaxanes are useful for gene transfection. Compared to conventional polymeric carriers they offer several advantages, such as modular assembly from well-defined building blocks, good biocompatibility and bio-degradability.</p>	
<p><b>References:</b></p> <ul style="list-style-type: none"> <li>[1] G. Wenz, <i>Angew. Chem. Int. Ed.</i> <b>1994</b>, <i>33</i>, 803.</li> <li>[2] A. Harada, M. Kamachi, H., <i>Macromolecules</i> <b>1990</b>, <i>23</i>, 2821.</li> <li>[3] G. Wenz, B.-H. Han, A. Müller, <i>Chem. Rev.</i> <b>2006</b>, <i>106</i>, 782.</li> <li>[4] G. Wenz, B. Keller, <i>Angew. Chem. Int. Ed.</i> <b>1992</b>, <i>31</i>, 197.</li> <li>[5] G. Wenz, C. Gruber, B. Keller, C. Schilli, T. Albuzat, A. Müller, <i>Macromolecules</i> <b>2006</b>, <i>39</i>, 8021.</li> </ul>	

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<b>Presentation Title:</b> Biотemplated Nanofabrication and Bioinspired Nanotechnology	
<b>Abstract:</b> <p>Nature provides abundant selections of micro- to nano-structures that can be used as templates for fabricating a wide range of photonic related structures. Replication is a method of using bio-templates for achieving nanostructures made of more stable, hard and high-temperature-tolerable inorganic materials that may have some designed functionalities for practical applications. Inorganic structures replicated from biological-template may combine the merits offered by both the materials and biological structures. We have replicated the photonic structures of butterfly wings using atomic layer deposition <sup>[1]</sup>. The reflectance spectra measurement demonstrates that the replica preserves not only the photonic property of the original butterfly wing, but also with tuneable color through a precise control over the thickness of the inorganic layer. Replication of fly eyes and water strider legs will also be presented <sup>[2,3]</sup>.</p>	
<p>The driving force for holding gecko lizards on a vertical solid surface to defy gravity comes from its remarkable feet and toes that are made of aligned microscopic elastic hairs. Using a rationally designed carbon nanotube arrays that are dominated by a straight body-segment but with curly entangled top, we have created gecko-foot-mimetic dry adhesives that showed the highest reported macroscopic adhesive force of <math>\sim 100 \text{ N/cm}^2</math>, almost ten times of that of a gecko foot (<math>10 \text{ N/cm}^2</math>) <sup>[4]</sup>. More importantly, these hierarchically-structured nanotube adhesives exhibited a much stronger shear adhesion force than the normal adhesion force (<math>\sim 10 \text{ N/cm}^2</math>) to ensure a strong binding along the shear direction and easy lifting in the normal direction. The mimetic adhesives can be alternatively binding-on and lifting-off for simulating the walking of a living gecko.</p>	
<b>References :</b>	
[1] J.Y. Huang, X.D. Wang, Z.L. Wang "Controlled replication of butterfly wings for achieving tunable photonic properties", <i>Nano Letters</i> , 6 (2006) 2325 - 2331.	
[2] Y. Ding, S. Xu, Y. Zhang, A.C. Wang, M.H. Wang, Y.B. Xiu, C.P. Wong, and Z.L. Wang "Modifying anti-wetting property of butterfly wings and water strider legs by biотemplated replication: surface materials verses geometry", <i>Nanotechnology</i> , 19 (2008) 355708.	
[3] J.Y. Huang, X.D. Wang, Z.L. Wang "Bio-inspired Fabrication of Antireflection Nanostructures by Replicating Fly Eyes", <i>Nanotechnology</i> , 19 (2007) 025602.	
[4] L.T. Qu, L.M. Dai, M. Stone, Z.H. Xia, Z.L. Wang "Carbon nanotube arrays with super-strong shear binding-on and easy normal lifting-off", <i>Science</i> , 322 (2008) 238-242.	

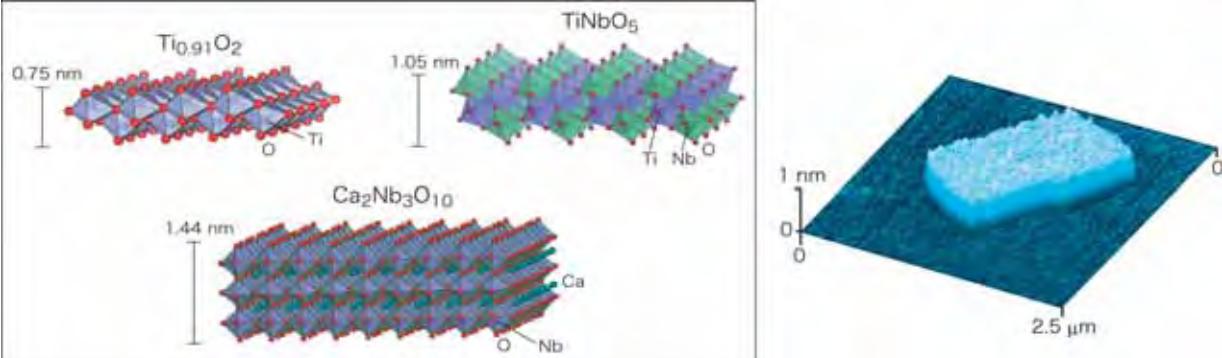
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<b>Presentation Title:</b> Molecular Beyonds	
<b>Abstract:</b> While design of nano-structured materials has already extensively investigated, polymeric materials composed of more than 2 monomeric components, with a controlled sequence, are still less explored. Especially, there is almost no reliable way to control the sequence of inorganic moieties, which is in sharp contrast to the case of pure organic analogues. Here we show our approach for the construction of metal ion arrays with a controlled sequence.	
In order to prepare controlled sequences of metal ions, we adopted solid phase synthesis technique as shown in the cartoon. We have synthesized organic templates bearing a ligand moiety. After metalation, the templates were coupled in a stepwise fashion on the surface of the resins. We will show the chain elongation capability of the templates as well as their applicability toward various metal ions.	
<b>References:</b> K. Heinze, M. Beckmann, K. Hempel, <i>Chem. Eur. J.</i> <b>2008</b> , 14, 9468.	

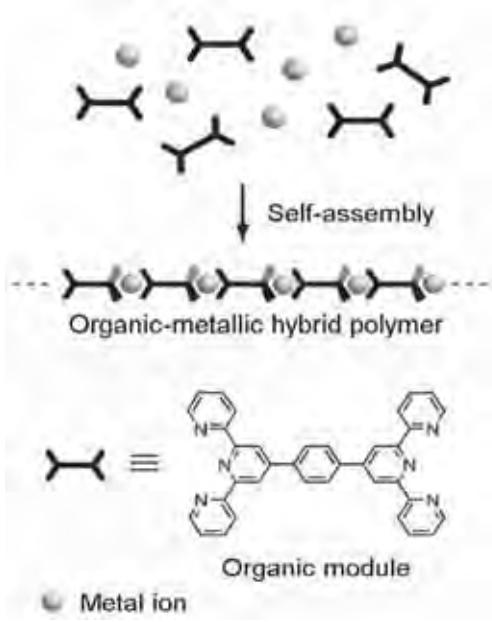
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<b>Presentation Title:</b> Toward higher performance permanent magnets for automotive applications	
<p>Interests in the coercivity mechanism of Nd-Fe-B based permanent magnets have recently been revived due to the increasing demand for high coercivity Nd-Fe-B based permanent magnets for automotive applications. To understand the microstructure-coercivity relationships of Nd-Fe-B magnets, we have investigated the microstructures of commercial and experimental sintered magnets and the hydrogen disproportionation desorption recombination (HDDR) powder by high resolution scanning electron microscopy, transmission electron microscopy and atom probe tomography. Continuous thin layers of a Nd-rich amorphous phase were found along the grain boundaries of optimally annealed sintered magnets, whose chemical composition was determined to be <math>Fe_{41}Nd_{33}Cu_{32}</math>, suggesting that the <math>Nd_2Fe_{14}B</math> grains are completely enveloped by a Cu and Nd enriched layer. Although the Nd-rich layer was also observed in the optimally processed HDDR powder, it was found to be crystalline with much less Nd-enrichment. Based on the information on the nanostructure feature of Nd-Fe-B magnets, we propose what we should do for developing higher coercivity Nd-Fe-B based magnets.</p>	
<p><b>References:</b></p> <ol style="list-style-type: none"> <li>1. W. F. Li, T. Ohkubo and K. Hono, <i>Acta Mater.</i> (2009) in press.</li> <li>2. W. F. Li, T. Ohkubo and K. Hono, <i>J. Mater. Res.</i> (2009), in press.</li> <li>3. W. F. Li, T. Ohkubo, K. Hono, T. Nishiuchi, and S. Hirosawa, <i>Appl. Phys. Lett.</i> 93, 052505 (2008).</li> </ol>	
<p>This work was supported by TOYOTA, CREST-JST, Rare Metal Substitute Materials Development Project on "Development of technology for reducing dysprosium usage in a rare-earth magnet", METI, Elements Science and Technology Project for "High performance anisotropic nanocomposite permanent magnets with low rare-earth content", and MEXT, Japan.</p>	



3DAP atom map of  $Nd_{12.5}Fe_{72.8}Co_{8.0}B_{6.5}Ga_{0.2}$  permanent magnet powder processed by the HDDR process

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<b>Presentation Title:</b> Electrical, mechanical properties and engineering of nanotubes, nanowires, nanobelts and nanocones in a transmission electron microscope	
<b>Abstract:</b> Diverse <i>in-situ</i> TEM experiments devoted to the analysis of electrical and mechanical properties, and engineering/manipulation of numerous individual inorganic nanostructures are presented. The STM-TEM and AFM-TEM holders integrated within a JEM-3100fef field-emission high-resolution transmission electron microscope are shown to be powerful tools in analysis of electrical conductance and elastic parameters of boron nitride nanotubes and nanocones, carbon and inorganic nanotubes filled with metals or ceramics, metal sulfide and nitride nanowires/nanobelts, and so forth <sup>[1]</sup> . The particular emphasis is put on the composite (metal/inorganic compounds in tubes) nanostructures mechanical performance, their morphology and property tuning under current-induced Joule heating. The local temperatures in the hot zones of the nanostructures were found to be high enough to allow melting of refractory metals, <i>e.g.</i> tungsten, and thermally robust compounds, <i>e.g.</i> BN. Figure 1 illustrates a so-called “nanopipette” made of a carbon nanotube initially filled with a copper halide, which has been melted and stepwise discharged from the tube interior onto the gold electrode, leaving copper nanodroplets behind <sup>[2]</sup> . The special attention is paid to the nanotube/metal heterojunctions formation inside TEM and analysis of the resultant electrical performances.	
	
<p>Fig. 1. A carbon nanotube pipette in action: copper nanodroplets (arrowed) are dripped on a gold electrode in designated positions when a <math>\mu</math>A range current is passed through a copper iodide-filled nanotube placed between two Au electrodes inside TEM (the counter-electrode is far to right)<sup>[2]</sup>.</p>	
<b>References:</b>	
[1] Golberg D. <i>et al.</i> “Properties and engineering of individual inorganic nanotubes in a transmission electron microscope”, <i>J. Mater. Chem.</i> (2009), in press, DOI: 10.1039/B814607A.	
[2] Costa P.M.F.J., Golberg D. <i>et al.</i> “Stepwise current-driven release of attogram quantities of copper iodide encapsulated in carbon nanotube”, <i>Nano Lett.</i> 8(10), 3120-3125 (2008).	

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<b>Presentation Title:</b> Oxide Nanosheets: New Solution to High-k Dielectrics	
<b>Abstract:</b> The integration of high permittivity ( $k$ ) dielectrics into microelectronic devices, combined with the size reduction constraints, is a current challenge in the semiconductor industry. In capacitor components, which form the basis of many memory devices, the static dielectric constant will ultimately decide the degree of miniaturization – a limit that is now being approached for the materials currently in use. In this talk, we report a “bottom-up” approach in which high-k dielectric nanofilms have been assembled from solution through the use of molecularly-thin oxide nanosheets as building blocks.	
A variety of oxide nanosheets (such as $\text{Ti}_{0.87}\text{O}_2$ , $\text{TiNbO}_5$ , $\text{Ti}_2\text{NbO}_7$ , $\text{Nb}_3\text{O}_8$ and perovskites) were synthesized by delaminating appropriate layered precursors into their molecular single sheets. These nanosheet only consists of $\text{TiO}_6$ and $\text{NbO}_6$ octahedra, a key building block of oxide dielectrics, which makes the nanosheet as an ideal base for high- $k$ dielectrics with the critical thickness. Layer-by-layer assembly was employed to fabricate high- $k$ dielectric nanofilms of these nanosheets on atomically-flat $\text{SrRuO}_3$ or Pt substrates. High-resolution transmission electron microscopy revealed that these multilayer nanofilms are composed of the well-ordered lamellar structure with an atomically sharp interface. These nanofilms exhibited both high dielectric constant ( $>200$ ) and low leakage current density ( $< 10^{-7} \text{ A/cm}^2$ ) for thickness down to 5 nm, contrasting to a size-induced dielectric collapse in typical high- $k$ films. Our results demonstrate a rational approach for building key nanoscale capacitors from oxide nanosheets, and thus represent a step towards a bottom-up paradigm for manufacturing of practical high- $k$ devices.	
	
Fig.1. Representative structures of high- $k$ dielectric nanosheets.	
<b>References :</b>	
1. M. Osada <i>et al.</i> , <i>Adv. Mater.</i> <b>18</b> , 1023-1027 (2006).	
2. M. Osada <i>et al.</i> , <i>Jpn. J. Appl. Phys.</i> , <b>47</b> , 7556-7560 (2008).	

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<b>Presentation Title:</b> Electrochromic Devices Using Organic-Metallic Hybrid Polymers	
<p><b>Abstract:</b></p> <p>Organic-metallic hybrid polymers are formed by complexation of organic modules and metal ions. Metallo-supramolecular polyelectrolytes (MEPEs), in which the organic modules are alternatively connected with the metal ions, are one of the organic-metallic hybrid polymers. Fe-MEPE has a purple color based on the metal-to-ligand charge transfer (MLCT) absorption from iron(II) ions to the terpyridyl units of the organic module. In cyclic voltammograms, a reversible wave is observed based on the redox between iron (II) and (III), and the half wave potential is at 0.77 V vs. Ag/Ag<sup>+</sup>. Interestingly, the polymer film cast on an ITO electrode using methanol shows electrochromic properties in acetonitrile: the purple film of the polymer becomes almost colorless, when a voltage of 2 V is applied to the electrode. Moreover, it is confirmed by <i>in situ</i> electro-spectroscopic measurements that the electrochromic changes in the hybrid polymers show high stability for the operations that are repeated more than 4,000 times. In addition, multicolor electrochromic changes appear on introducing two kinds of metal ions to the polymer. We also succeeded in fabricating an electrochromic solid-state device by using these polymers as shown in the right figure.</p>	
 <p>The diagram illustrates the self-assembly process. At the top, several organic modules (represented by a stylized Y-shaped structure) and metal ions (represented by small grey spheres) are shown separately. An arrow labeled "Self-assembly" points downwards, indicating the formation of the polymer structure. The resulting "Organic-metallic hybrid polymer" is shown as a chain of alternating organic modules and metal ions. Below this, a chemical structure of the "Organic module" is provided, showing a central benzene ring with three terpyridyl ligands attached. A legend indicates that the grey spheres represent "Metal ion".</p>	
 <p>A photograph showing a person's hands working on a piece of equipment, likely a vacuum沉积 apparatus, used for fabricating the electrochromic solid-state device. The equipment has "NIMS" and "NIMS" logos on it.</p>	
<p><b>References:</b></p> <p>Proc. Natl. Acad. Sci. USA, <b>103</b>, 10202 (2006); Chem. Rec., <b>7</b>, 203 (2007); Adv. Mater., <b>19</b>, 3928 (2007); J. Am. Chem. Soc., <b>130</b>, 2073 (2008); J. Mater. Chem., <b>18</b>, 4555 (2008).</p>	

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<b>Presentation Title:</b> Intelligent nanostructured surface for cell sheet tissue engineering	
<b>Abstract:</b> Ideal tissue construction in vitro and in vivo should be achieved by cell and cell sheet manipulation engineering that would be established with the following three core technologies: first, the noninvasive harvest of cultured cells and cell sheets are realized with our developed temperature-responsive culture dishes. The surfaces are hydrophobic at 37° C, but change to hydrophilic below 32° C. Various cell lines adhere, spread and proliferate on the surfaces similarly to those on commercial tissue culture dishes. Only by reducing temperature, cells spontaneously detached from the surfaces without the need for trypsin. Confluent cells are also recovered as a single contiguous monolayer sheet with intact cell-cell junctions and deposited extracellular matrix. <sup>1, 2)</sup> Second, the harvested viable cell sheets can be transferred to other surfaces of culture dishes or devices (2D cell sheet manipulation) because the extracellular matrix associated with the basal side of cell sheets shows adhesion. Thus, tissue regeneration with cell sheet tissue engineering can be accomplished either by transplantation of single cell sheets, as with skin, cornea <sup>3)</sup> and periodontal ligaments. <sup>4)</sup> Finally, the recovered cell sheets can be stratified to reconstruct complex stratified tissue architectures such as liver lobule <sup>5, 6)</sup> , kidney glomeruli <sup>7)</sup> , and cardiac patches (3D cell sheet manipulation). <sup>8)</sup> For example, layered cardiomyocyte sheets harvested from temperature responsive dishes pulsate simultaneously and show diffuse gap junction formation. When transplanted into the subcutaneous tissues of nude rats, spontaneous beatings could be macroscopically observed and maintained for over 1 year. We have initiated clinical study of tissue engineering therapy using heart patch for cardiomyopathy.	
<b>References :</b>	
1) M. Yamato et. al., <i>Materialstoday</i> , <b>May 2004</b> , 42-47(2004). 2) J. Yang et. al., <i>MRS Bulletin</i> , <b>30</b> (3), 189-193 (2005). 3) K. Nishida et. al., <i>N. Engl. J. Med.</i> , <b>351</b> (12), 1187-1196 (2004). 4) T. Akizuki et. al., <i>J. Periodont. Res.</i> , <b>40</b> (3), 245-251 (2005). 5) M. Harimoto et. al., <i>J. Biomed Mater Res.</i> , <b>62</b> (3):464-70(2002). 6) K. Ohashi et. al., <i>Nat. Med.</i> , <b>13</b> (7), 880-885(2007). 7) A. Kushida et. al., <i>J. Biomed. Mater. Res.</i> , <b>54</b> (1):37-46(2001). 8) T. Shimizu et. al., <i>Circ. Res.</i> , <b>90</b> (3):e40-48(2002).	

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<b>Presentation Title:</b> Detection of biomolecular recognition using bio-transistors	
<p><b>Abstract:</b>            We have proposed the novel concept of a genetic field effect transistor (FET) which is based on direct transduction of surface density change of charged biomolecules into electrical signal by the field effect<sup>1</sup>. We combined a genetic FET with specific molecular recognition such as allele specific hybridization, intercalation, and primer extension to detect one base difference of target DNA.</p> <p>The conceptual structure of a genetic FET is shown in Fig. 1. Oligonucleotide probes are immobilized on the surface of the gate insulator. The genetic FET is immersed in a measurement solution together with an Ag/AgCl reference electrode with saturated KCl solution. The photograph of the fabricated FET chip is shown in Fig. 2.</p> <p>The cycle of single-base extension and measurement of the <math>V_T</math> was repeated iteratively to determine the base sequence of the target DNA. As a result, the positive <math>V_T</math> shifts could be detected in accordance with the base sequence of the target DNA. Thus, the results of iterative extension reaction and detection of the threshold voltage indicated the ability of a direct, simple and potentially high throughput DNA sequencing analysis using the FETs.</p> <p>We also propose an oocyte-based field effect transistor (oocyte-based FET) for drug transport analysis, in which target transporters are expressed at the cell membrane of the oocyte. Non-invasive monitoring of the uptake kinetics of substrates mediated by membrane-bound transporters can be realized with oocyte-based FET.</p>	
<p><b>References:</b>            T. Sakata and Y. Miyahara, DNA sequencing based on intrinsic molecular charges, <i>Angewandte Chemie International Edition</i>, 45, 2225-2228 (2006).</p>	

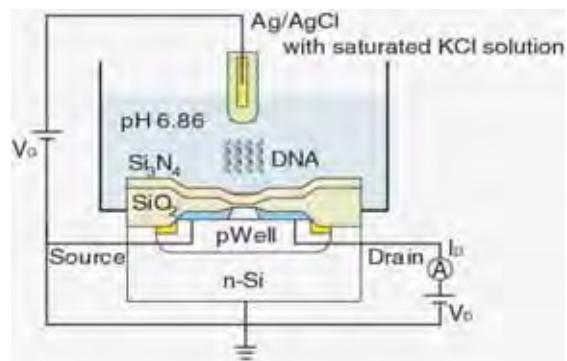


Figure 1 Schematic diagram for measurements of electrical characteristics of genetic FET.

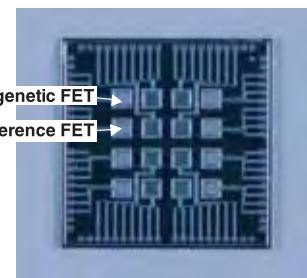


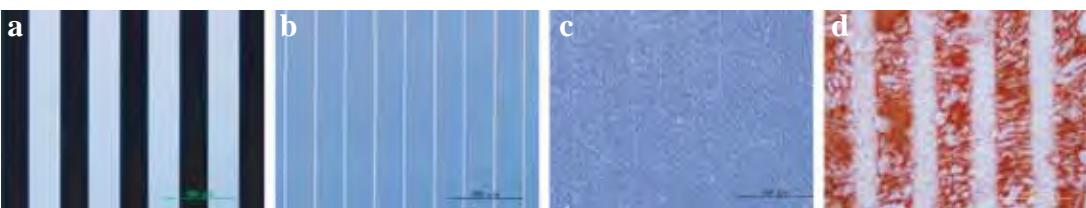
Figure 2 Photograph of the fabricated genetic FET chip. Sixteen FETs and a temperature sensor are integrated in a 5 mm x 5 mm chip.

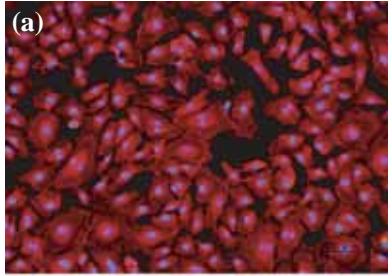
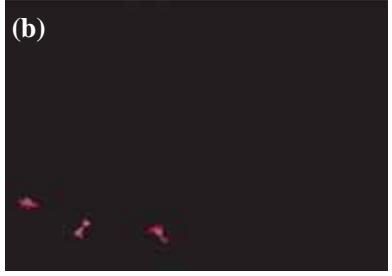
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<b>Presentation Title:</b> Biocompatibility evaluation of bioabsorbable magnesium alloys	
<b>Abstract:</b> <p>Magnesium (Mg) and its alloys were first applied to orthopaedic implants in early 20's century, but recent attempts on stent application open a new stage as a bioabsorbable metal. However, available biocompatibility data of Mg and its alloys is restricted. Since Mg generates H<sub>2</sub> and OH<sup>-</sup> along the progress of its corrosion reaction with water, the pH of the fluid around Mg surface will increase, which may affect surrounding cellular and tissue function. In this study, biocompatibility of Mg and its alloys is examined by cell culture method in vitro.</p> <p>The materials used are pure Mg, AZ31, AZ61, and AZ80. The disks of 9.5 mm in diameter or the plates of 8 x 9 mm and 2 mm in thickness were prepared. Every surface of these specimens was polished with #600(14μm) SiC paper and washed with acetone. Murine fibroblast L929 were seeded at the concentration of 1000 cells/mL in Eagle's minimum essential medium supplemented with 10 % (v/v) of fetal bovine serum and cultured in a 5%(v/v) CO<sub>2</sub> incubator for 1, 4, and 7 d. Then, the number of viable cells was estimated by WST-1 assay. Mg<sup>2+</sup> in the culture medium was quantified by a colorimetric method.</p> <p>The highest cell growth was observed for AZ31, followed by pure Mg. Cell growth was very low for AZ61 and AZ80. The highest release of Mg<sup>2+</sup> was observed for pure Mg, followed by AZ31, AZ61, and AZ80 in the order. This indicates that corrosion reaction is more active at the surface of pure Mg rather than those of AZ61 and AZ80. Therefore, the lower cell growth at the surface of AZ61 and AZ80 is not simply attributed to the increase of pH of the fluid near the specimen surface due to corrosion reaction. In the case of aluminum (Al)-containing Mg alloys, Al condensation in the surface oxide layer was observed after immersion into NaCl solution <sup>[1]</sup>. It is also reported that PVD film of pure Al has lower cell attachment and survival ratio than those of glass <sup>[2]</sup>. These facts suggest that higher content of Al may reduce the cell attachment and growth on Al-containing Mg alloys.</p>	

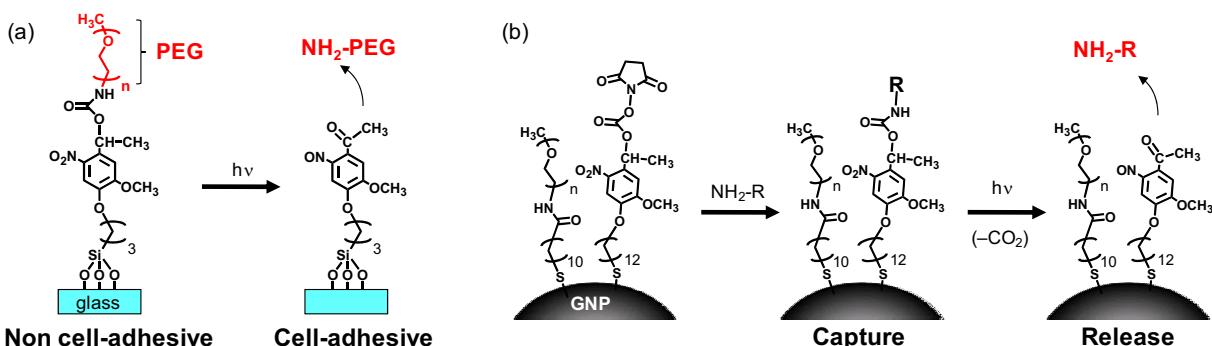
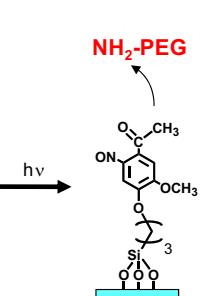
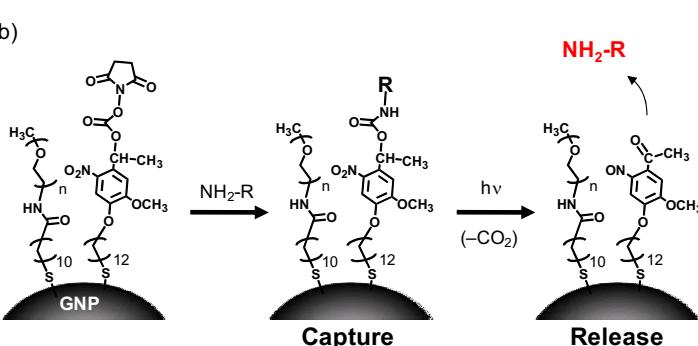
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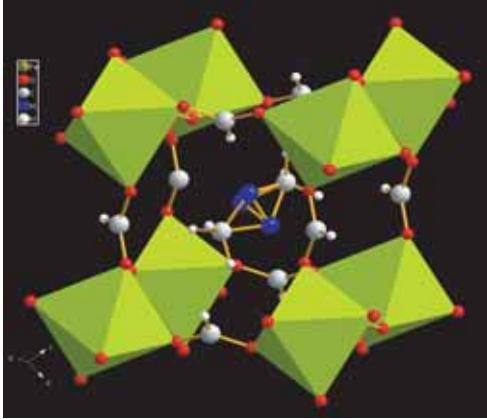
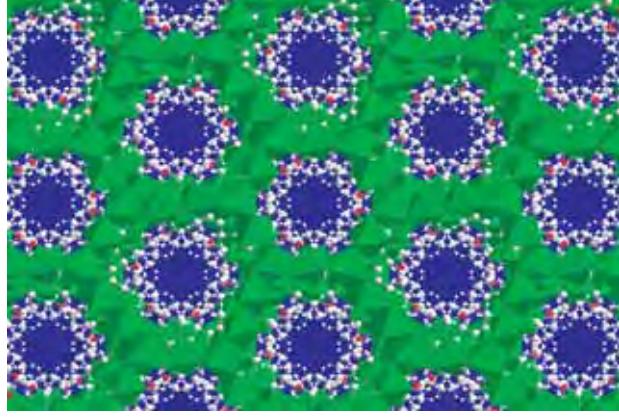
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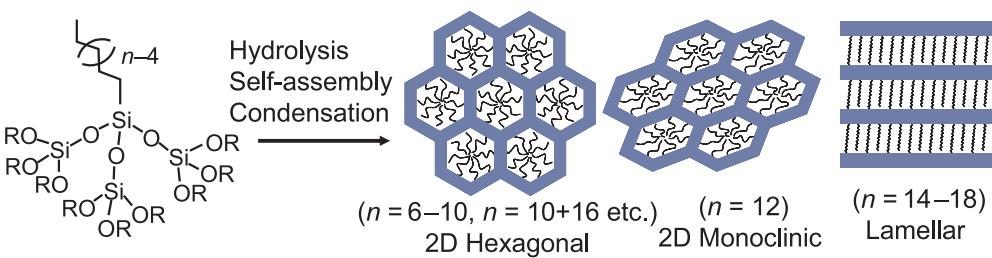
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<b>Presentation Title:</b> Nano-particle Assisted Therapy	
<b>Abstract:</b> Nanosized polymeric particles have versatile utilities such as carrier for drug delivery, bioimaging and nano-diagnostic system. Recently, we have been focusing on preparation of core-shell type polymeric nanogels, which possess crosslinked polyamine core and biocompatible poly(ethylene glycol) (PEG) shell. The obtained nanogel showed volume phase transition in a minute change in environmental pH. Using the nanogel thus prepared as a nanoreactor, new nanomaterials were prepared for new therapy and imaging tools.	
Recently, we have found that gold nanoparticles (GNPs) were successfully synthesized through the self-reduction of Au(III) ions with PEGylated nanogels composed of polyamine gel core and PEG chains <sup>1</sup> . TEM images revealed that the synthesized GNPs located only in the nanogel core, indicating that nanogel acted as both nanoreactor and nanoreservoir for GNPs. Additionally, number of GNPs in single nanogel could be easily arranged by changing N / Au (number of amino groups / number of Au atoms) ratio. The obtained gold nanoparticle containing nanogels (GNG) were applied for an enhancement of cancer photothermal therapy as well as radiotherapy in response to electromagnetic wave in cultured cancer cells.	
Cancer photothermal effect was tested using HeLa cells ( $10^5$ cells / well) after treatment with GNG(1) ( $[\text{Au}] = 168 \mu\text{g} / \text{mL}$ ). Figure 1 shows fluorescence microscopy image of double-stained HeLa cells after irradiation of $\text{Ar}^+$ laser (514.5 nm, 51mW / $\text{cm}^2$ , $d = 1 \text{ mm}$ ) for 5 min. As can be seen in Figure 1, dead cells (red fluorescence) were clearly observed only in the laser irradiation-region (inner of yellow circle), whereas the living cells (green fluorescence) were only observed out of the laser irradiation-region. This result strongly indicates that pinpoint cancer photothermal therapy was successfully achieved using GNG. Radiotherapy was carried out using A549 cells (200 cells / dish in case of 4 Gy irradiation sample) after treatment with GNG(2) ( $[\text{Au}] = 15 \mu\text{g} / \text{mL}$ ) or the PEGylated nanogels without GNPs. The results of giemsa-stained colony assay of A549 cells showed that the number of the colony decreased after irradiation of 4, 8, 12, 16 Gy of X-ray (200 kV, 20 mA, 4 Gy / min). These results clearly show that GNG acted as an efficient radioenhancer, which may reduce the side effect of cancer radiotherapy. In conclusion, noninvasive photothermal and radiotherapy were successfully achieved using GNG as electromagnetic enhancer.	 <p>Fig.1 Fluorescence microscope image of double-stained HeLa cells after laser irradiation.</p> <p>TEM of Gold-containing Nanogel</p>
This study was carried out by group of Nagasaki Laboratory in University of Tsukuba collaborated with Prof. Matsuishi Lab in U.Tsukuba and Prof.Inanami in Hokkaid U. The author appreciates, Professors K.Matsuishi, O.Inanami, M.Oishi, Drs. H.Yasui and H.Hayashi, Messrs. A.Tamura, T.Nakamura, Y.Jinji and R.Takeuchi for their collaboration of this study.	
<b>References:</b> M. Oishi, H. Hayashi, T. Uno, T. Ishii, M. Iijima, and Y. Nagasaki, <i>Macromol. Chem. Phys.</i> , 208, 1176-1182 (207).	

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<b>Presentation Title:</b> Manipulation of Stem Cell Functions by Patterned Polymer Surfaces	
<b>Abstract:</b> <p>Manipulation of stem cell functions is an important technique for tissue engineering. It was realized by patterned surfaces. Gelatin was pattern-grafted on cell-culture polystyrene plate surface and used for culture of human mesenchymal stem cells (MSCs). The pattern was prepared by UV-irradiating the photoreactive azidobenzoyl-derivatized gelatin-coated surface of a polystyrene plate through a photomask with 200-<math>\mu</math>m-wide stripes. The MSCs adhered on both polystyrene and gelatin-grafted surfaces, proliferated to reach confluent. The cells were stained with alkaline phosphatase (ALP) and alizarin red S (calcium staining) to analyze the osteogenic differentiation of MSCs on these surfaces. The cells on both polystyrene and gelatin-grafted surfaces were positively stained by alkaline phosphatase. No pattern stain of alkaline phosphatase was detected. However, the cells on gelatin-grafted surface were strongly stained by alizarin red S after two weeks culture, while cells on polystyrene surface very weakly stained after two weeks culture. Therefore the alizarin red S staining followed the gelatin pattern. The pattern became less distinct after three weeks culture, and not evident after four weeks culture. The MSCs showed osteogenic differentiation pattern following the gelatin pattern in the first three weeks. Gene expression analyses using real-time PCR indicated that MSCs cultured on the gelatin-grafted surface showed higher level of genes encoding alkaline phosphatase and bone sialoprotein than did on polystyrene surface. The expression of gene encoding osteocalcin was at almost the same level for both surfaces. These results suggest that the osteogenic differentiation rate of MSCs on the polystyrene and gelatin-grafted surfaces were different, and that the MSCs differentiated more quickly on the gelatin-grafted surface than did on the polystyrene surface. The pattern surface could be used to control differentiation of stem cells, and may be used to reconstruct the complex structure of tissue and organs.</p>	
	
<p>Fig. 1. Photomicrographs of photomask (a), PVA-patterned polystyrene surface (b), and MSCs cultured on the PVA-patterned surface in osteogenic induction medium for 2 weeks without staining (c) and stained with alizarin red S (d).</p>	
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<b>Presentation Title:</b> Novel Biointerface with Well-Defined Concentrated Polymer Brushes Obtainable by Surface-Initiated Living Radical Polymerization.		
<b>Abstract:</b> <p>Surface-initiated living radical polymerization has been used to graft well-defined polymers with an extremely high graft density, and such densely grafted polymers have been classified into the “concentrated” polymer brush, giving characteristic structure and properties: for example, these brushes are surprisingly highly extended in a good solvent, providing strong resistance against compression, ultra-low friction (or super lubrication), and size exclusion with a limit set for a very low molecular weight.[1] Focusing the unique structure and properties of concentrated brushes, we aim to develop, by utilizing the advantages of surface-initiated LRP, a concentrated brush-based novel biointerface that would precisely control biological reactions, e.g., protein adsorption, cell-adhesion, and so on. For this goal, we planned to elucidate the mechanism of interactions between concentrated brushes and biomolecules such as protein and cells.</p>	 	
<p>First, we systematically investigated protein adsorption by quartz crystal microbalance as a function of graft density (the graft density <math>\sigma = 0.01, 0.1</math>, and <math>0.7</math> chains/nm<math>^2</math>) and protein size (2 - 13 nm in an effective diameter <math>2R_g</math>). We exhibited that excellent protein repellency of the concentrated poly(2-hydroxyethyl methacrylate) (PHEMA) brush (<math>\sigma = 0.7</math> chains/nm<math>^2</math>), and this was reasonably ascribed to the unique structure of concentrated polymer brushes.</p> <p>Then, we examined HUVEC and platelet adhesions on PHEMA brushes with different graft densities (<math>\sigma = 0.1</math> and <math>0.6</math>). PHEMA is often used for modification of inner surface of an artificial blood vessel, however its blood compatibility is still needed to improve. As we expected, HUVEC and platelet adhesions were little observed on the concentrated brush compared to the semi-dilute one. Furthermore, we also investigated protein and cell adhesions on other hydrophilic concentrated brushes. The details will be discussed.</p>		
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<b>Presentation Title:</b> Photoresponsive Biointerfaces for Cell Analysis	
<p><b>Abstract:</b>          Biointerface is an interface between biomolecules and materials. We have been developing photoresponsive biointerfaces for controlling cellular functions as well as for engineering tissue mimics <i>in vitro</i>.</p> <p><b>Photoactivatable cell culture substrate.</b><sup>[1]</sup> Activities of the cells are highly dependent on their microenvironment, as can be imagined from the complex architecture of tissues and organs. However, most cell researches have been conducted on normal plastic or glass dish, whereon cells were attached quite randomly. We have developed several photoactivatable cell culture substrates that changed from non-cell-adhesive to cell adhesive in response to light (<b>Figure 1a</b>). Based on this feature, we were able to produce arbitral cell patterns by controlled irradiation. Furthermore, we succeeded in inducing cell migration and proliferation by irradiation during cell cultivation.</p> <p><b>Photoresponsive nanocarrier.</b><sup>[2]</sup> Concentrations of biomolecules such as hormones and proteins in living system are strictly controlled both in time and space. Therefore, it is important to deliver such biomolecules at will not only for therapeutic purposes but also for studying intertwined inter- and intracellular signal transduction networks. We have developed colloidal gold nanoparticles (GNPs) presenting a photocleavable succinimidyl ester that allows for the delivery of amine derivatives (<b>Figure 1b</b>). Under this molecular design, the GNPs capture the amine derivatives on their surfaces and release them upon irradiation at any desired time and space. As a proof of concept, we synthesized histamine-immobilized GNPs and examined their ability to evoke intracellular signaling by fluorescence imaging.</p>	
 <p><b>(a)</b> <b>Non cell-adhesive</b> </p> <p><b>(b)</b> <b>Capture</b> </p>	
<p>Figure 1. Photoresponsive Biointerfaces. (a) Change in cell adhesiveness on a photoactivatable cell culture substrate. (b) Capture and release of amine derivatives (<math>\text{NH}_2\text{-R}</math>) on photoresponsive gold nanoparticles (GNPs).</p>	
<p><b>References:</b></p> <ul style="list-style-type: none"> <li>[1] J. Nakanishi <i>et al.</i> <i>J. Am. Chem. Soc.</i>, 129, 6694, 2007; Y. Kikuchi <i>et al.</i> <i>Chem. Lett.</i>, 37, 1062, 2008.</li> <li>[2] J. Nakanishi <i>et al.</i> <i>submitted</i>.</li> </ul>	

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<b>Presentation Title:</b>	Recent Developments in Hybrid Inorganic-Organic Framework Materials		
<b>Abstract:</b>	<p>The study of hybrid inorganic-organic frameworks is one of the most fashionable areas of materials science. The presentation will focus on some aspects of our recent work on hybrid framework, which may be nanoporous or dense. The synthesis of carboxylates and imidozalates will be described, and we shall examine the energetic and other factors that control structural trends in such materials [1-2]. We shall also examine some of the potential applications of hybrid materials in areas such as enantiomerically-selective catalysis, hydrogen storage, magnetism, photoluminescence, and multiferroics [3-6].</p>		
 			
<b>References:</b>	<ol style="list-style-type: none"> <li>1. A. K. Cheetham, C. N. R. Rao and R. K. Feller, <i>Chem. Comm.</i> 4780 (2006)</li> <li>2. A. Bailey, C. Lee, R. K. Feller, J. B. Orton, C. Mellot-Draznieks, B. Slater, W. T. A. Harrison, P. Simoncic, A. Navrotsky, M. C. Grossel, and A. K. Cheetham <i>Angew. Chem. Int'l. Ed. Eng.</i> 47, 8634 (2008).</li> <li>3. A. K. Cheetham and C. N. R. Rao, <i>Science</i>, 318, 58 (2007)</li> <li>4. C. N. R. Rao, A. K. Cheetham and A. Thirumurugan, <i>J. Phys. Cond. Matter</i> 20, 083202 (2008).</li> <li>5. P. Jain, N. S. Dalal, B. H. Toby, H. W. Kroto, and A. K. Cheetham, <i>J. Amer. Chem. Soc.</i> 130, 10450 (2008).</li> <li>6. M. Kosa, M. Krack, A. K. Cheetham and M. Parrinello, <i>J. Phys. Chem. C</i> 112, 16171 (2008).</li> </ol>		

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<b>Presentation Title:</b> Control of Composition, Structure, and Morphology of Mesostructured Materials	
<p><b>Abstract:</b>            Mesostructured and mesoporous materials have attracted great interests as a key material for science and technology for the next generation. The composition, structure, and morphology of the materials are diverse, which widens the potential applications of these materials.</p> <p>In this presentation, the significance of the formation of mesostructured and mesoporous materials will be discussed. Several concepts, such as self-assembly, templating, inorganic-organic interactions, etc., are involved in the preparation of this type of materials. Such mesoscale design is strongly related to biomimetic processing of materials. In order to clarify the implication of this group of materials, the compositional, structural, and morphological controls of mesostructured materials will be presented.</p> <p>One of the topics to be covered is the precise design of the inner pore environment. A possible solution for this issue is the molecular design of precursor. Recent results in the synthesis of mesostructured silica-based materials based on self-assembly of amphiphilic alkoxy silane precursors are interesting. A variety of ordered hybrid materials have been obtained from newly synthesized precursors. Alkoxy silanes with covalently attached hydrophobic organic tails are hydrolyzed to form amphiphilic molecules containing silanol groups, leading to the formation of mesostructures. Hydrolysis and condensation of molecules having alkyl chains and oligosiloxane heads (<math>C_nH_{2n+1}Si(OSi(OMe)_3)_3</math>) lead to the formation of mesophases consisting of cylindrical assemblies, providing a direct pathway to ordered porous silica.(Fig. 1) Further increase in the head group leads to the formation of a 3D mesostructure which has cage-type mesopores. Morphological and hierarchical controls of silica-based mesostructures by utilizing the precursors will also be presented.</p>	
	
<p>Fig. 1 Self-assembly process of <math>C_nH_{2n+1}Si(OSi(OMe)_3)_3</math></p>	

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<b>Presentation Title:</b> PERSPECTIVES OF NANO-SPINTRONICS	
<b>Abstract:</b> <p>Nano-spintronics is based on three important pillars: I) metal-based multilayer systems and nanostructures, finding applications in GMR and TMR sensors as well as advanced magnetic storage media, II) semiconductor-ferromagnet heterostructures and diluted magnetic semiconductors, which promise to extend the capabilities of semiconductor-based nanoelectronics, and III) molecular-based spintronics, which is currently emerging and having the greatest potential in terms of miniaturization and functionality. However, advances in all three areas depend critically on a fundamental understanding of magnetic and spin-dependent properties and interactions at the atomic level, requiring the determination of spin structures and spin excitations down to the atomic scale. The direct visualization of atomic-scale spin structures [1-4] has first been accomplished for magnetic metals by combining the atomic resolution capability of Scanning Tunnelling Microscopy (STM) with spin sensitivity, based on vacuum tunnelling of spin-polarized electrons [5]. The resulting technique, Spin-Polarized Scanning Tunnelling Microscopy (SP-STM), nowadays provides unprecedented insight into collinear and non-collinear spin structures at surfaces of magnetic nanostructures and has already led to the discovery of new types of magnetic order at the nanoscale [6,7]. More recently, the development of sub-Kelvin SP-STM has allowed studies of ground-state magnetic properties of individual magnetic adatoms on non-magnetic substrates as well as the magnetic interactions between them [8]. Moreover, the detection of spin-dependent exchange and correlation forces has allowed a first direct real-space observation of spin structures at surfaces of antiferromagnetic insulators [9]. This new type of scanning probe microscopy, called Magnetic Exchange Force Microscopy (MExFM), offers a powerful new tool to investigate different types of spin-spin interactions based on direct-, super-, or RKKY-type exchange down to the atomic level. By combining MExFM with high-precision measurements of damping forces, localized or confined spin excitations in magnetic systems of reduced dimensions now become experimentally accessible. Finally, the combination of spin state read-out and spin state manipulation, based on spin-current induced switching across a vacuum gap by means of SP-STM [10], provides a fascinating novel type of approach towards ultra-high density magnetic recording without the use of magnetic stray fields.</p>	
<b>References:</b>	
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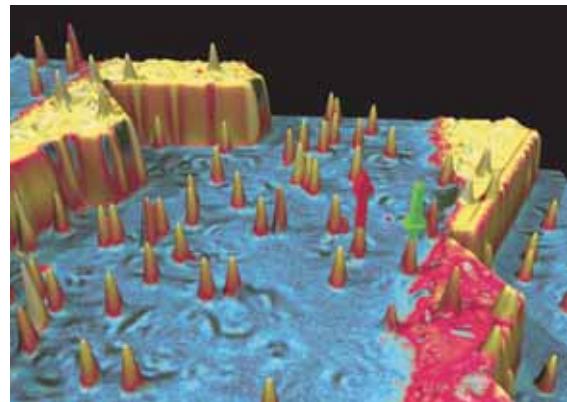
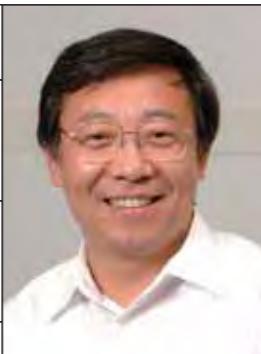
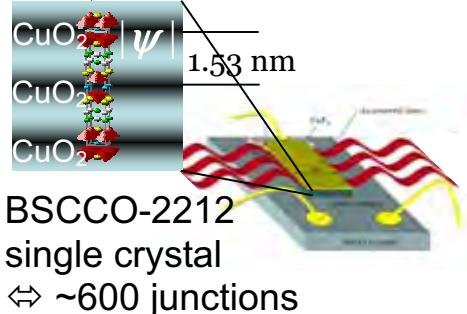


Fig. 1. Individual Co adatoms on a stepped Pt(111) substrate and Co monolayer stripes attached to the Pt step edges. The STM topograph has been colorized with the simultaneously recorded spin-resolved  $dI/dU$  map measured with a magnetic tip being sensitive to the out-of-plane spin component.

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<b>Presentation Title:</b> MANA-CNSI Overview	
<b>Abstract:</b> <p>I will discuss the progress in two topical areas of the MANA project at CNSI at UCLA. First is the work on growth of fractal networks of silver for creating atomic switch arrays. Here we have been working on the functionalization of fractal networks with sulfide connections, the switching characteristics of which resemble a synapse. Second I will discuss work on non-contact AFM in liquids for high resolution imaging of biological objects with dimensions in the sub-100nm regions. These include vaults which are self-assembled proteins structures found in all cells and exosomes which are lipid-protein-RNA containing structures. We will focus on the mechanical considerations of imaging these at low force and correlate our data with TEM uranyl nitrate and staining with gold antibody beads. An update of the UHV nc-AFM for the MANA brain will also be covered.</p>	
<h2>MANA NN-3</h2> <ul style="list-style-type: none"><li>• Ag/Ag<sub>2</sub>S/Ag nanowire interfaces – 2 wire layers</li><li>• fast &amp; simple process for fabrication of nanoscale switching contacts</li><li>• coupled switching between multiple individual Ag/Ag<sub>2</sub>S/Ag interfaces</li></ul>  	

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<b>Presentation Title:</b> Nano Superconductivity as a Novel Source of THz Electromagnetic Wave	
<b>Abstract:</b> Electromagnetic (EM) waves, ranging from the rf waves to $\gamma$ ray, are deeply related with the daily life. Below the visible lights, there locates the so-called terahertz ( $=10^{12}$ Hertz, THz) band. The EM waves in this range are very useful for genetic analysis, material inspection and telecommunication, to name a few. Quantum cascade lasers based on super lattice of semiconductors only provide THz EM waves in the pulse form and of fixed frequency, although the power is fairly large. To seek continuous and strong sources of the THz EM waves is still a matter of scientific challenge.	
Superconductivity provides a unique way to generate THz radiation due to the famous Josephson relations: when a finite voltage is applied across two superconducting electrodes with a thin gap (Josephson junction), the phase difference across the junction evolves with time in a velocity proportional to the voltage (ac Josephson relation), and huge number of Cooper pairs proportional to the sinusoidal function of the phase difference tunnel across the junction (dc Josephson relation). The tunneling of Cooper pairs is accompanied by the emission of photons, or equivalently EM waves. A voltage of 1mV emits the EM wave at about half of 1THz.	 <p>BSCCO-2212 single crystal <math>\Leftrightarrow \sim 600</math> junctions</p>
Soon after the discovery of cuprate high-Tc superconductivity, it was demonstrated that a single crystal of layered superconductors, such as $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ , behaves as a stack of intrinsic Josephson junctions (IJJs). The IJJs are closely packed with a period of 1.5 nm, and their homogeneity is guaranteed by the crystal structure down to the atomic scale, both very ideal for getting strong radiations.	
The challenge in exciting strong radiation is then to operate all the junctions coherently. One way to achieve coherence is to build a cavity by a mesa of BSCCO single crystal. The cavity resonance of the Josephson plasma will then force all the Josephson junctions to oscillate in phase. By large-scale computer simulations and theoretical analysis on a model described by the coupled sine-Gordon equations with large inductive coupling, we found that a novel dynamic state can be stabilized by injecting c-axis dc currents, in which a $\pi$ phase kink appears around the junction center [1,2]. According to our estimate, this novel state can pump dc energy into THz radiations with energy density larger than other known states by three orders.	
This work is a collaboration with S.-Z. Lin and is supported by WPI Initiative on Materials Nanoarchitectonics, MEXT and CREST, JST, Japan.	
<b>References:</b>	
[1] S.-Z. Lin and X. Hu, Phys. Rev. Lett. vol. 100, 247006 (2008)	
[2] X. Hu and S.-Z. Lin, Phys. Rev. B, vol. 78, 134510 (2008)	

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**Presentation Title:**

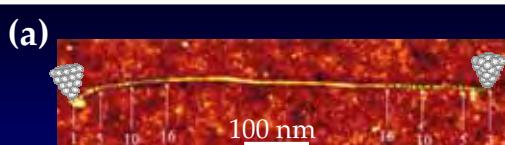
Nanoscale Electrical Transport Measurement by Multiple-Scanning-Probe Microscopes

**Abstract:**

Signal transfer in nanoscale materials is getting more important for realizing nanoscale devices and understanding functionality of nanocomposites. For this purpose, multiple probes for inputs and outputs of signals are set within nanoscale distance as nanosized signal sources using home-built multiple-scanning-probe microscopes (MP-SPMs) [1]. The MP-SPMs use probes as electrodes for making contact with a single nanostructure of interest and each probe can obtain surface features in an atomic scale. In this presentation, we show electrical measurements of various nanostructures, such as single-walled carbon nanotubes (SWCNTs) using MP-SPMs.

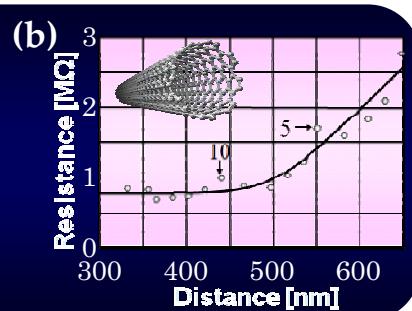
Electrical transport through SWCNTs was examined by two-probe-type MP-SPM. The resistance ( $R$ ) of a SWCNT was repeatedly measured between the two contacting probes with changing the interprobe distance ( $L$ ) [Fig. 1(a)]. The measured resistances decreased along with approximation of the two probes down to 500 nm, whereas they were kept constant at the interprobe distance below 500 nm [Fig. 1(b)]. This result is in good agreement with the length of electron mean free path in SWCNT of several hundred nm even at room temperature as theoretically predicted. We also report other experimental examples of MP-SPM measurement and newly developed probes which can be utilized even at the interprobe distance below 100 nm [2]. Measurement must be performed in various environments, especially on insulating substrate. We already have started the extension of our MP-SPM to multiple-scanning probe “atomic force microscope”. We expect that MP-SPM can make novel approach to understand functionalities of various materials such as organic molecules and nanocomposites.

**Fig.1**

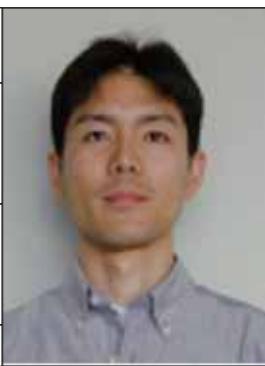
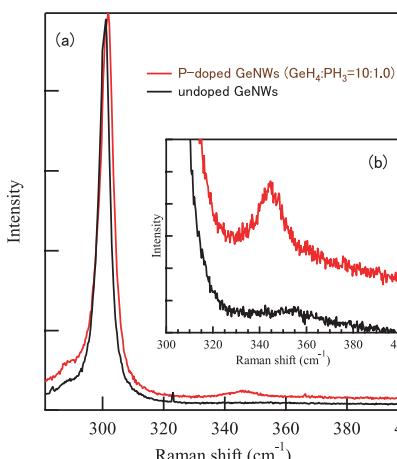


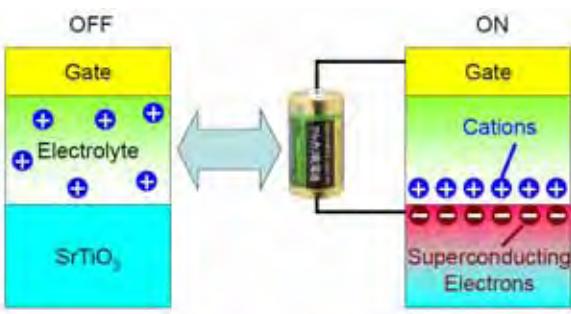
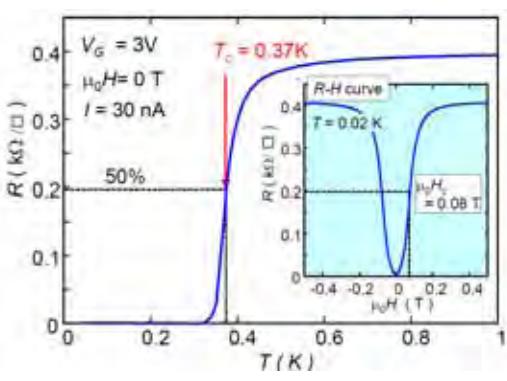
(a) 680 x 110 nm<sup>2</sup> STM image of an isolated SWCNT.

(b) R-L plot of the SWCNT showing slope changes at the interprobe distance below 500 nm.

**References:**

- [1] M. Aono, C.-S. Jiang, T. Nakayama, T. Okuda, S. Qiao, M. Sakurai, C. Thirstrup, and Z.-H. Wu, *Oyo Buturi* **67**, 1361 (1998). (in Japanese).
- [2] O. Kubo, Y. Shingaya, M. Nakaya, M. Aono, and T. Nakayama, *Appl. Phys. Lett.* **88**, 254101 (2006).

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<b>Presentation Title:</b> Synthesis and impurity doping into germanium nanowires as the basis for next-generation semiconductor devices	
<b>Abstract:</b> A considerable amount of work has been done regarding one dimensional semiconductor nanowires. In particular, silicon nanowires (SiNWs) have gained attention since such SiNWs-based nanodevices are desirable for their compatibility with the present Si complementary metal-oxide semiconductors (Si CMOS) integrated circuit technology and offer better scalability and leakage control. Germanium (Ge) is considered to be more desirable materials for the next-generation metal-oxide semiconductor field-effect transistors (MOSFETs) since electron and hole mobilities in Ge are higher than those in Si, indicating potential performance gains compared to Si-based devices. Recently, we could succeed in clarifying the states of boron (B) and phosphorus (P) atoms in SiNWs. In this talk, the states of B and P atoms doped in Ge nanowires (GeNWs) were investigated by micro-Raman scattering measurements.	
GeNWs were grown on a Si(111) substrate by a chemical vapor deposition (CVD) reactor using a 10 sccm of GeH <sub>4</sub> (100%). The total pressure was set at 7 Torr by mixing a N <sub>2</sub> gas. Doping of B and P were performed during the growth. Diborane was used the p-type dopant and phosphine as the n-type dopant. Gold nanocolloid particles with 3 nm in diameter were used as seed for vapor-liquid-solid growth of GeNWs. The substrates with the gold nanocolloids were heated at 300-350°C. Micro-Raman scattering measurements were performed at room temperature with a 100x objective and a 532-nm excitation light at a power of 0.02 mW.	 Fig. 1 SEM and TEM images of GeNWs.
SEM and TEM images of GeNWs are shown in Fig. 1. The TEM image shows that the core is crystalline Ge and the surrounding layer is amorphous GeO <sub>2</sub> with 2 nm in thickness. Local vibrational peaks of B and P atoms in GeNWs were clearly observed at 546.3 and 345.0 cm <sup>-1</sup> , respectively. The result for P-doped GeNWs is shown in Fig. 2. Asymmetric broadening due to the Fano effect was also observed in the Ge optical phonon peak. These results show that the B and P atoms were doped into the crystalline Ge core of GeNWs and electrically activated in the substitutional sites, resulting in the formation of p-type and n-type GeNWs.	 Fig. 2 Raman spectra observed for P-doped and undoped GeNWs.
<b>References:</b> [1] N. Fukata et al., Appl. Phys. Lett. <b>89</b> (20), 203109 (2006). [2] N. Fukata et al., Appl. Phys. Lett. <b>90</b> (15), 153117 (2007).	

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<b>Presentation Title:</b> Electric Field Induced Superconductivity in an Insulator	
<b>Abstract:</b> <p>Tuning the electric properties of solids has been and will be the most important method in electronics. Since the field effect transistors (FET) was invented in 1940's, the size of devices has been shrunk to push up the integration density. However, maximum charge density that can be accumulated in a solid surface through gate insulator has not been improved much. One of the biggest challenges in materials science has been to induce superconductivity by electric field but the charge density had not been high enough to make the phase transition possible.</p> <p>We have demonstrated that, for the first time, an insulator could be turned by electric field into metal with superconducting transition at low temperature. The material of choice is <math>\text{SrTiO}_3</math> that is known as an insulator with high dielectric constant. <math>\text{SrTiO}_3</math> is also known as an n-type semiconductor that can be doped into degenerated state by chemical substitution. Degenerated <math>\text{SrTiO}_3</math> shows superconductivity at an electron density above <math>10^{18} \text{ cm}^{-3}</math>, which is the lowest carrier density among known superconductors. The maximum critical temperature (<math>T_c</math>) is 0.4K at <math>10^{20} \text{ cm}^{-3}</math>. If the carriers distributed at the surface region of 10nm, the areal charge density corresponds to <math>10^{14} \text{ cm}^{-2}</math> that is higher than maximum attainable value in conventional FET by a few orders of magnitude.</p> <p>To solve this problem, we employ an electric double layer structure to form a capacitor the surface of <math>\text{SrTiO}_3</math>. Polyethylene-oxide solvent containing <math>\text{KClO}_4</math> electrolyte was used and the Helmholtz double layer was formed by applying a voltage of a few volts (Fig. 1). Electrons of up to <math>10^{14} \text{ cm}^{-2}</math> are accumulated on the surface to induce superconductivity at about 0.4K (Fig. 2).</p>	
	
Fig. 1 A schematic of superconducting FET	Fig. 2 Low temperature characteristics of a field induced superconductivity.
<b>References:</b>	
1. K. Ueno, et. al., <i>Nature Materials</i> , 7, 855-858 (2008)	

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Spin-polarized Carrier Injection Effect in a Ferromagnetic Semiconductor/Diffusive Semiconductor/Superconductor Junction

**Abstract:**

We report the transport properties in a p-In<sub>0.94</sub>Mn<sub>0.06</sub>As/n-InAs/Nb junction where a p-InMnAs can be regarded as a spin injector [1]. We discuss both experimentally and theoretically the way in which the competition between the spin polarization and superconducting proximity effect modifies the transport in our systems.

We measured the bias voltage V dependence of the differential conductance of the n-InAs channel as a function of injection current from p-InMnAs at 0.7 K and 20mK.

We obtained conductance minima within |V|<2 mV without current injection.

As the injection current from p-InMnAs increased, the conductance minima gradually disappeared (Fig. 1 (b)).

By contrast, as the injection current from Nb increased, the conductance minima split and then shifted toward a high bias (Fig. 1(a)).

In the calculation of the conductance in the n-InAs channel we solved both the Usadel equation and the gap equation self-consistently by taking account of the exchange field in the InAs channel that was induced by InMnAs ferromagnetic electrode.

The difference between the dependences of the conductance on injection current can be explained by the inverse proximity effect that the exchange field is also induced in the superconducting electrode by spin-polarized current injection from the InMnAs electrode.

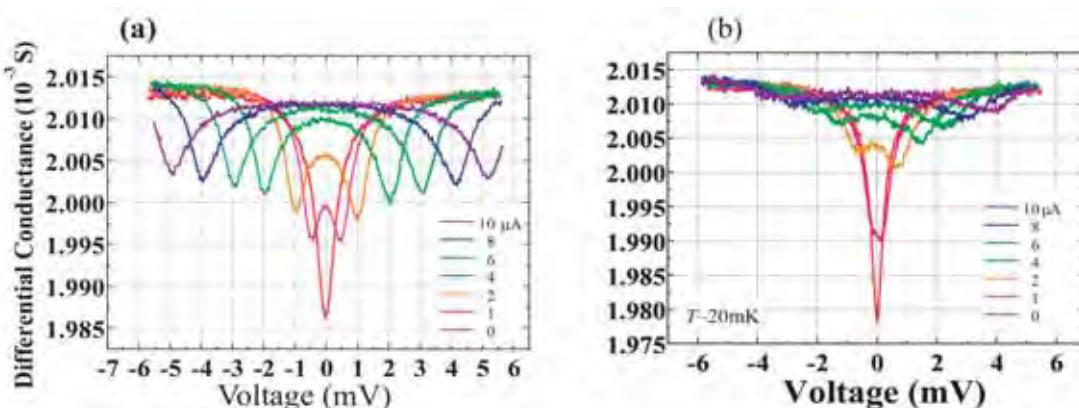
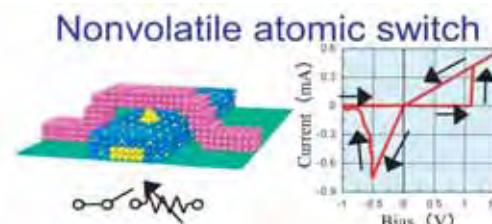
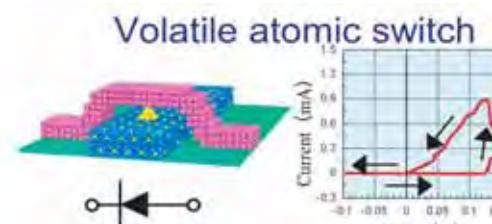
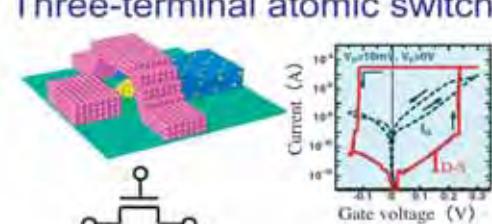
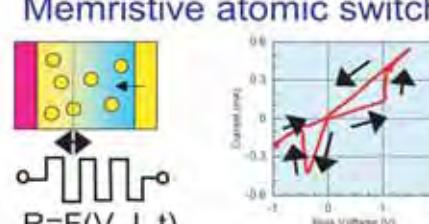


Figure 1. The bias voltage V dependence of the differential conductance of the n-InAs channel between two Ti/Au electrodes as a function of injection current (a) from Nb and (b) from p-InMnAs at 20 mK.

**References:**

[1] T. Akazaki et al., to be published in the Proceedings of LT-25 (in Journal of Physics: Conference Series).

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<b>Presentation Title:</b> Atomic switch for neural networking systems	
<b>Abstract:</b> The atomic electronic device has a possibility for configuring new computing systems, such as non-Boolean logic systems. For instance, the atomic electronic device is non-volatile, which enables simultaneous logical operation and memorization by a single device. The characteristic could enable for configuring the logic system, which changes by itself according to the logical operation. Namely, conceptually new type of nonvolatile-logic circuit such as neural networking systems may be developed.	
Variety kinds of functions are required to configure the neural networking systems. We found that the atomic switch can achieve several functions by modifying device structures and using different materials. Figure 1 shows examples of the novel functions of the atomic switch. For instance, atomic switch with a metal source in the solid-electrolyte electrode works as nonvolatile switch. Without a metal source, it becomes volatile switch. The atomic switch also has learning ability. In the presentation, these functions for configuring new computing systems are introduced with their characteristics.	
<p><b>Nonvolatile atomic switch</b></p> 	<p><b>Volatile atomic switch</b></p> 
<p><b>Three-terminal atomic switch</b></p> 	<p><b>Memristive atomic switch</b></p>  <p><math>R = F(V, I, t)</math></p>
Figure 1 Variety kinds of functions of atomic switch.	
<b>References:</b> K. Terabe, T. Hasegawa, T. Nakayama and M. Aono, <i>Nature</i> <b>433</b> (2005) 47.	

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**Presentation Title:**

Connection of Conductive Molecular Nanowires to Single Functional Molecules

**Abstract:**

In order to realize future nanophotonic or nanoelectronic devices, the use of single functional molecules as light emitters or electronic switches will be a good candidate. For making electric connections to individual functional molecules, a method to wire single molecules with conjugated organic polymers is required. We have developed a method using a probe tip of scanning tunneling microscope (STM) to control the chain polymerization of diacetylene compounds on a self-ordered layers, thereby creating single nanowires of conjugated polydiacetylene<sup>1-3</sup>. Using this method, we will demonstrate here the connection of polydiacetylene nanowires to metal-phthalocyanine (Me-Pc) molecules.

10,12-Nonacosadiynoic acid [ $\text{CH}_3(\text{CH}_2)_{15}\text{C}\equiv\text{CC}\equiv\text{C}(\text{CH}_2)_8\text{COOH}$ ] was used as a diacetylene compound, and Me-Pc was deposited on a layer of diacetylene on a graphite substrate. STM experiments were performed in air at room temperature.

We found that stable nano-clusters, which were consisted of single to few Me-Pc molecules, were adsorbed on the diacetylene layer. Especially, nano-clusters consisted of five Me-Pc molecules (pentamer) were frequently observed. The connection of molecular nanowires to a Me-Pc pentamer is demonstrated in Fig. 1. A chain polymerization was initiated by applying a pulsed bias voltage on a diacetylene molecular row toward a pentamer using a tip of STM. As a result, the chain polymerization of diacetylene was propagated toward the pentamer, and terminated at the site of Me-Pc. We applied another pulsed bias voltage to the other side of diacetylene molecular row, which initiated a chain polymerization as well and also terminated at the site of Me-Pc. As a result, we could connect two polydiacetylenes to the single Me-Pc molecule in the pentamer.

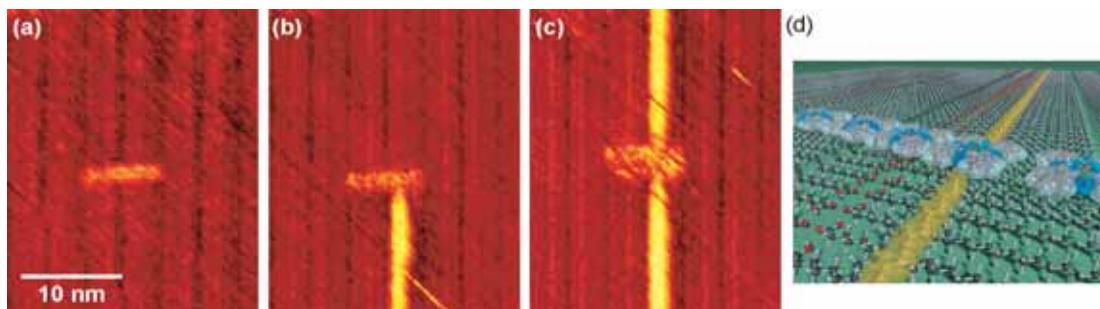
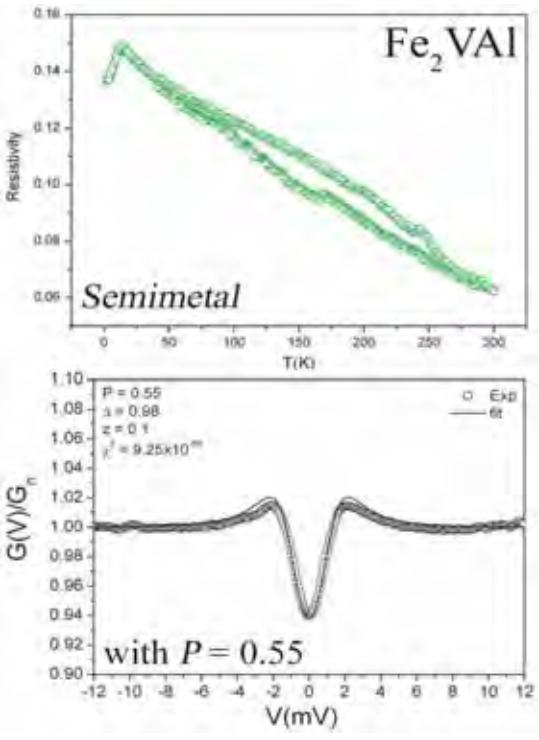
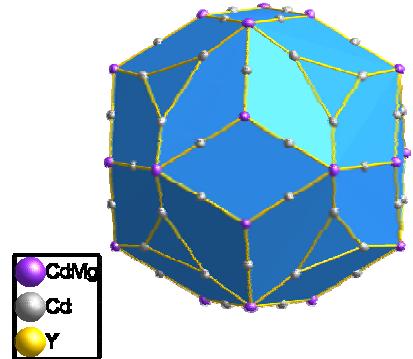


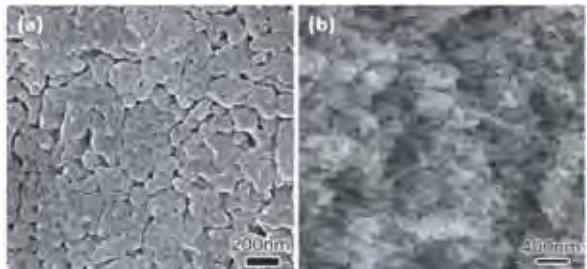
Fig. 1 Connection of molecular nanowires to Me-Pc pentamer.

**References:**

- [1] Y. Okawa, M. Aono, *Nature* 409 (2001) 683.
- [2] Y. Okawa, M. Aono, *J. Chem. Phys.* 115 (2001) 2317.
- [3] D. Takajo, Y. Okawa, T. Hasegawa, M. Aono, *Langmuir* 23 (2007) 5247.

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<b>Presentation Title:</b> Engineering the properties of Heusler alloys for spintronic devices.	
<b>Abstract:</b> Half-metals are the materials in which spin up electrons are metallic and spin down electrons are semiconducting in nature. These half-metallic materials have attracted intense attention as key materials for realizing spintronic devices of all types, including giant magnetic resistance (GMR) devices for read heads in hard disk drive (HDD), tunnel magnetoresistive (TMR) devices for magnetoresistive random access memory (MRAM) and others.	
Direct measurement of the spin polarization of ferromagnetic materials is possible using Andreev reflection. The amount of suppression in Andreev reflection depends on the intrinsic spin polarization of materials [1]. For applications in spintronic devices we need high $T_c$ half-metallic materials with high spin polarization. In this aspect Co-based Heusler alloys have several advantages over others [2].	
Recently Co-Mn based Heusler alloys have found its applications in GMR devices because of their high resistance area product (RA) values [3]. These alloys have high $T_c > 800^\circ\text{C}$ and high magnetization $> 4\mu_\text{B}$ . Further more due to magnon excitations the temperature dependent decay of MR values for these devices is an obstacle for practical applications. We proposed Nd doped $\text{Co}_2\text{MnSi}$ to be a potential candidate for applications as it was found that Nd doping drastically reduces the magnon excitations.	
Low magnetic moment with high spin polarization and with considerable amount of magnetic anisotropy is required for domain wall memory switches. Some of the Fe based Heusler alloys whose magnetic moment is relatively low (0.1 to $0.3\mu_\text{B}$ ) also has some interesting technological implications. In this talk I will be discussing the importance of Heusler alloys in various spintronic devices and the materials that we developed at NIMS.	
<b>References:</b>	
1. R. J. Soulen et al. Science 282 85 (1998). 2. I. Galanakis, P. H. Dederichs, and N. Papanikolaou, Phys. Rev. B 66, 174429 (2002). 3. T. Furubayashi, K. Kodama, H. Sukegawa, Y. K. Takahashi, K. Inomata, and K. Hono, Appl. Phys. Lett. 93, 122507 (2008).	

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<b>Presentation Title:</b> Chemical order in Ternary Complex Metallic Alloys	
<b>Abstract:</b> Complex metallic alloys such as quasicrystals are compounds which are still far from being efficiently used in applications because of our inability to completely understand their structures and properties. The question that has haunted scientists in quasicrystal research from the very beginning has been "where are the atoms?". Not until very recently has this question been answered for the case of a binary icosahedral quasicrystal in the Yb-Cd system.[1] However, most quasicrystals are not binary but ternary, and thus often suffer from partial chemical order/disorder. This chemical order must be understood if we wish to gain complete structural understanding of quasicrystals and approximants, and we must thus answer a second question: "which atom is where?".	
In this work we present the results of analyses made on chemical order of several ternary Yb-Cd type approximants. The experimental results are based on X-ray diffraction experiments using several special techniques such as anomalous scattering and combined simultaneous powder/single crystal refinements. The experimental results clearly show that when Cd in the parent RE-Cd approximants is replaced by atom pairs such as Ag/In, Au/Sn and Cd/Mg the new atom pairs do not randomly distribute themselves over the previous Cd atom positions. In some cases certain sites are reserved for specific elements while other sites allow chemical mixing. It is known that Hume-Rothery mechanisms can explain the relative compositions of quasicrystals and approximants by considering factors such as atomic size and e/a ratios. However for the detailed understanding of chemical order at the atomic level, these mechanisms are not sufficient and thus other factors must be considered as well. A theoretical approach has been attempted by calculating total energies using DFT in order to understand the underlying reason for the experimentally observed chemical order.	 <p>Fig1. Partial chemical order between Cd and Mg in a ternary Y-Mg-Cd quasicrystal approximant.</p>
<b>References :</b> [1] H. Takakura*, C. Pay Gómez, A. Yamamoto, M. de Boissieu, A. P. Tsai Nature Materials. 2007, 6, 58.	

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<b>Presentation Title:</b> Nano structured materials design with phase separation	<b>Abstract:</b> The phase separation has been extensively studied both experimentally and theoretically.[1] The phase separation is observed in mixtures of various types of condensed matter such as liquids, metals, polymers, and glasses. Due to the presence of immiscibility, the phase separating systems present a unique opportunity for designing composites with hierarchical microstructure at different length scales and provide opportunity for developing materials with unique properties. For example, phase separating silicate glasses are well known and are widely studied for scientific understanding and technological exploitation such as Vycor and Pyrex glasses. Additionally, to understand the phase separation mechanism can give an opportunity to design the nano porous materials. Porous metallic materials have been used in lots of fields including aerospace, electrochemistry, petrochemistry, medicine and substitute energy related research. Their distinctive structures make them very useful as lightweight structural materials, separation membranes, catalyst supports, impact energy absorbers, acoustic dampeners, and heat exchangers.[2] But there are still many challenges to improve the properties of porous materials with controlling the porous size and shape. In present study, we designed the phase separating FeCu and CoCu binary system with thermodynamic calculation. From the calculated critical composition, the interconnected phases are observed in melt spun ribbon sample. The perfectly interconnected metallic porous materials could be synthesized from the separated two different phases by the selective dissolution method. Because the difference of chemical activity of separated phases, Fe rich, Co rich, and Cu rich phases were selectively dissolved in the nitric acid. Finally, the iron based in Fig. 1. the cobalt based and Cu based metallic porous materials have been formed. The synthesized porous ribbon could be used as a membrane supporter that can reduce the thickness of Pd layer for hydrogen separation.
	
<b>References:</b> [1] B. J. Park et al., Phys. Rev. Lett., 96, 245503 (2006) [2] J. Banhart, Prog. Mater. Sci. 46, 559 (2001)	

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<b>Home Page:</b>	
<b>Presentation Title:</b> Templated synthesis of electrically conductive organic materials	
<b>Abstract:</b> Possibility of controlling morphology of polymer chains in conductive polymeric materials is presented. The conductive polymer was synthesized as nanowires using porous alumina templates, and the electrical measurements on the individual nanowires revealed that the template size will affect the resistivity of resulting nanowires.	
The polymeric nanowires of poly(3,4-ethylenedioxythiophene) (PEDOT) were synthesized by the electro-polymerization of 3,4-ethylenedioxythiophene (EDOT) monomers within the porous alumina template.[1] The size of the template can determine the diameter of the synthesized PEDOT nanowires (30~200nm). Electrical measurements on the individual PEDOT nanowires using a nano-probing system (Fig.1) show that the nanowires with the smaller diameter have the lower resistivity. We expect that the nano-sized template can improve the morphology of polymer chains, resulting in the better conductivity of resulting polymeric materials. Our synthesis methodology using the porous alumina template will provide a practical route for synthesizing polymeric materials suitable for plastic electronics.	 N-6000 2.0kV x30 0k SE 1.00um
<b>References:</b> [1] Xiao, R.; Il Cho, S.; Liu, R.; Lee, S. B., Controlled electrochemical synthesis of conductive polymer nanotube structures. <i>J. Am. Chem. Soc.</i> <b>2007</b> , 129 (14), 4483-4489	

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<b>Presentation Title:</b> Nanopatterning Self-Assembling Polymers	
<b>Abstract:</b> <p>In the past decades of fabrication of structures and devices on surfaces, much progress has been made. Mass-produced electronics have moved from the micron-scale regime to the nanoscale regime. There is an imbalance, however, in current methods; control over patterning and structure fabrication is significantly more advanced in lateral directions than it is in the vertical direction.<sup>1-4</sup> If we were to make an analogy of transistors in circuits to people in cities, we are trying to build Tokyo with only one-story buildings. Traditional photolithography is not amenable to vertical fabrication because of the typical top-down implementation. This has given rise to the idea of bottom-up nanofabrication. In accordance with this idea, we have prepared a series of polymers that can grow from a templated surface, reproducing the initial structure with aspect ratios &gt;10 without degrading feature size. By alternating polymers and their derivative functionalities, we can fabricate nanoscale structures in the vertical direction.</p>	
 S4800 10.0kV 7.8mm x45.0k SE(M) 1.00μm	
<b>References:</b> (1) Hurley, P. T.; Ribbe, A. E. R.; Buriak, J. M. <i>J. Am. Chem. Soc.</i> <b>2003</b> , <i>125</i> , 11334-11339. (2) Maoz, R.; Frydman, E.; Cohen, S. R.; Sagiv, J. <i>Advanced Materials.</i> <b>2000</b> , <i>12</i> , 424-429. (3) Xia, Y.; Kim, E.; Mrksich, M.; Whitesides, G. M. <i>Chem. Mater.</i> <b>1996</b> , <i>8</i> , 601-603. (4) Lee, M. V.; Nelson, K. A.; Hutchins, L.; Becerril, H. A.; Cosby, S. T.; Blood, J. C.; Wheeler, D. R.; Davis, R. C.; Woolley, A. T.; Harb, J. N.; Linford, M. R. <i>Chem. Mater.</i> <b>2007</b> , <i>19</i> , 5052-5054.	

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<b>Presentation Title:</b> Development of high field superconducting magnets	
<p><b>Abstract:</b>            Applications for high field superconducting magnets are accelerators, fusion research, laboratory magnet and NMR spectroscopy. At the present time the limit for superconducting magnet is about 21 T, because of the intrinsic properties of Nb<sub>3</sub>Sn (the main material for building superconducting magnets), but higher fields are strongly demanded. For example, in NMR magnets higher magnetic fields are needed to obtain higher resolution.</p> <p>The High Temperature superconducting materials could generate much higher magnetic field, and a 23 T magnet was already tested in 2005. Recently, the new YBa<sub>2</sub>Cu<sub>3</sub>O<sub>x</sub> coated conductors have attracted the interest of magnet builders, because of the remarkable mechanical and superconducting properties.</p> <p>In this work the electro-mechanical properties (critical current versus field and mechanical stress) of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>x</sub> tapes have been studied. In particular, the dependence of the critical current from the angle between the magnetic field and the tape normal was measured. Moreover the mechanical limit (hoop stress) was determined on jointed tapes, single turn and multi-turns coils.</p> <p>A new procedure for designing superconducting magnets is introduced, taking into account the improved properties and the unique characteristics of the HTS conductors.</p> <p>Test coils (Fig.1) have been designed and are under construction.</p>	
<p><b>References :</b></p> <p>D. Uglietti and T. Kiyoshi, “Optimization of the Superconducting and Mechanical Properties of Conductors for High Field Solenoid Magnets”, to be published in IEEE Trans. on App. Supercond. Vol. 19 (2009).</p> <p>T. Kiyoshi et al., “Generation of high magnetic fields using superconducting magnets”, Fusion Engineering and Design Vol. 81 (2006) 2411.</p> <p>M. Beckenbach et al., “Manufacture and Test of a 5 T Bi2223 Insert Coil”, IEEE Trans. on App. Supercond. Vol. 15 (2005) 1484.</p>	



Fig. 1 Superconducting coil before testing

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<b>Presentation Title:</b> Three-dimensional Imaging with Confocal Scanning Transmission Electron Microscopy	
<b>Abstract:</b> <p>Three-dimensional (3D) imaging has been an indispensable technique in various industrial and scientific fields. Recently, confocal scanning transmission electron microscopy (STEM), which is based on applying the principles of confocal imaging to transmission electron microscopy, has attracted considerable interest as a promising depth-sectioning and 3D imaging technique [1,2]. Figure 1 shows a schematic drawing of the confocal STEM configuration. Depth sectioning can be performed by rejecting electrons from an out-of-focal plane in a specimen (broken lines). However, 3D imaging with confocal STEM has not yet been established because of practical difficulties. In this work, we developed a stage-scanning system for STEM in order to overcome the difficulties and applied to confocal imaging. By using the system, only the specimen is moved three-dimensionally under the fixed lens configuration. A specimen holder with a piezo-driven stage was modified and controlled by computer programming for stage scanning. Detected signals are synchronized with the specimen displacement and are displayed on a computer screen as a stage-scanning STEM image, as shown in Fig.1. Observation of gold particles demonstrated that the developed system is capable of atomic-resolution STEM imaging at desired Z positions. Further, confocal STEM images could be obtained under the confocal lens configuration. Details of the stage-scanning system and obtained results will be discussed.</p>	
<b>References :</b> [1] N. J. Zaluzec, Microsc. Today Vol. 6 (2003) 8-12. [2] P. D. Nellist, G. Behan, A. I. Kirkland, and C. J. D. Hetherington, Appl. Phys. Lett. Vol. 89 (2006) 124105.	

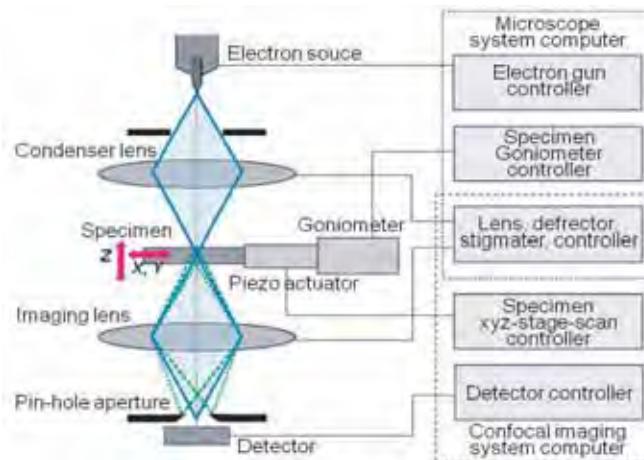
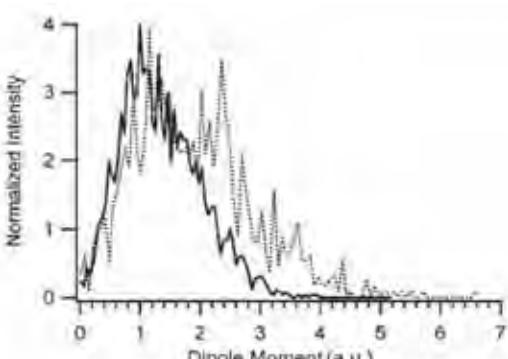
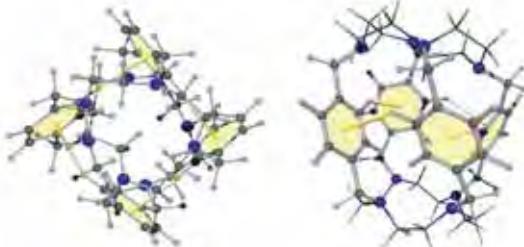


Fig.1 Illustration of the confocal STEM configuration and stage-scanning system.

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<b>Presentation Title:</b> <i>Ab initio</i> Molecular Dynamics: an atomic-scale simulation approach to nanoscience and nanotechnology	
<b>Abstract:</b> In Materials Science, modeling is necessary in order to interpret experimental results as well as predict new trends in experimental research. Molecular dynamics is an atomic-level description of the evolution of different systems (gas, liquids bulk solids and surfaces) at different thermodynamic conditions. Ab-initio molecular dynamics has the power of describing these molecular systems without the limitations of empirical potentials, electrons being treated explicitly at quantum mechanics level and forces on atoms computed from the full Hamiltonian.	
Car-Parrinello molecular dynamics uses electrons and ions on the same level as simultaneously time-evolving lagrangean variables, thus avoiding the cost of wavefunction recalculations at each step.	
In this talk I show the power of Car-Parrinello Molecular Dynamics applied to different systems: from water solution, where NaCl solutions have been compared to pure water [1], to the description of new organic molecules complimentary to fullerenes [2] to functionalization of Carbon Nanotubes [3]. This technique can become an indispensable virtual laboratory for materials modeling and materials architectonics for theoreticians and experimentalists alike.	
	
Fig 1. Distributions of dipole for water molecules for pure water (dashed) and a solution containing 0.43 M of NaCl (solid) (from [1]).	Fig 2 New found molecular structure of $C_{48}N_8H_{64}$ confirmed using ab initio finite temperature Car Parrinello Molecular Dynamics (from [2]).
<b>References:</b>	
<p>1] R. Scipioni, D. Schmidt, M. Boero, J. Chem Phys. <b>130</b> 024502 (2009).      2] J. Hill, R. Scipioni, M. Boero et al, Phys. Chem. Chem Phys. (submitted).      3] M. Pumera, R. Scipioni, H. Iwai, et al. Chem. A Europ. J (submitted).</p>	

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## Presentation Title:

## Bacterial Electron Transfer and Electricity Generation in the Genus *Shewanella* : A Strategy to Improve Current Generation

## Abstract:

It was first shown more than 90 years ago that microorganisms can generate electricity in a course of metabolism. This has attracted much recent attentions for its application in biological fuel cells. However, serious problems of low current density of this system compared to the existing platinum- or enzyme-based chemical fuel cells have prevented them from being applied in energy production systems for practical use. We found that this problem can be solved essentially by introducing the bacteria/semiconductor network on electrode surfaces. Herein we report the *c*-Cyt-mediated ET from *Shewanella loihica* PV-4 to semiconducting  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> film electrodes, and the subsequent findings of drastic improvements of microbial current generation achieved by the self-constructed *Shewanella*

Extracellular ET from *Shewanella loihica* PV-4 to ITO electrode was studied using a single-chamber three-electrode system with lactate being used as a carbon source and an electron donor. A flat ITO glass was used as a working electrode. The current was generated immediately after adding the suspension of condensed cells into the reactor. The current increased gradually with time and reached a constant value. It is likely that the current generation was a consequence of direct electrical connections of the cells to the ITO electrode, followed by the injection of electrons from *c*-Cyt to the electrode.

It is to be noted that the current, however, showed practically no dependence on the cell density. *In-situ* optical microscope observation of the ITO electrode revealed that the surface was completely covered with the cells and there were abundant planktonic cells in the reactor solution. This implies that the current generation from *S. loihica* are dominated by the cells attached directly to the electrode surface. In turn, inefficient long-distance ET processes of *S. loihica* is a main reason for low current density of this system.

Upon adding the  $\alpha\text{-Fe}_2\text{O}_3$  colloids, however, the current showed a steep rise until reaching the maximum value at approximately 50 times larger. SEM observation revealed the formation of thick layers composed of cells and colloids, in which the outer surfaces of the cells are covered with the  $\alpha\text{-Fe}_2\text{O}_3$  colloids. These results suggest that the drastic enhancement (> 300-fold) of the redox currents is due to the interconnection of *S. loihica* through  $\alpha\text{-Fe}_2\text{O}_3$  network acting as ET conduits, which enables a number of cells located at a long distance from the electrode

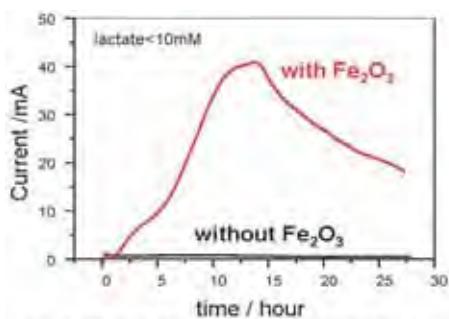


Fig. 1 Effect of addition of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> colloids on microbial current generation by *S. loihica*. The  $I$  vs.  $t$  curves measured in the presence and absence of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> colloids (7.5 mM)

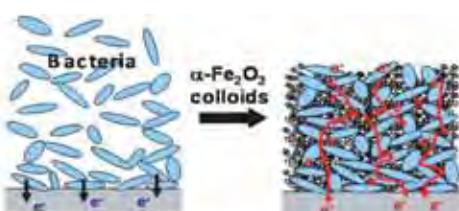
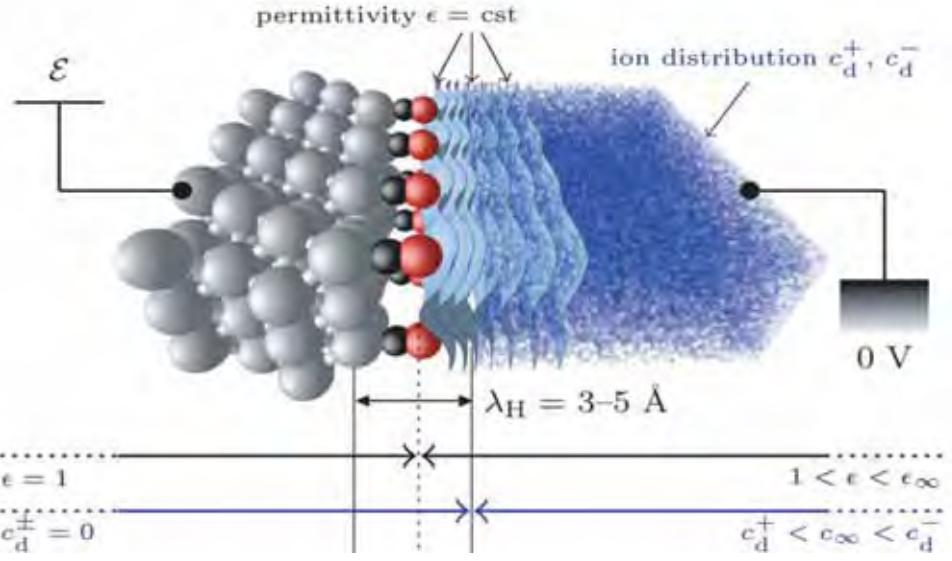
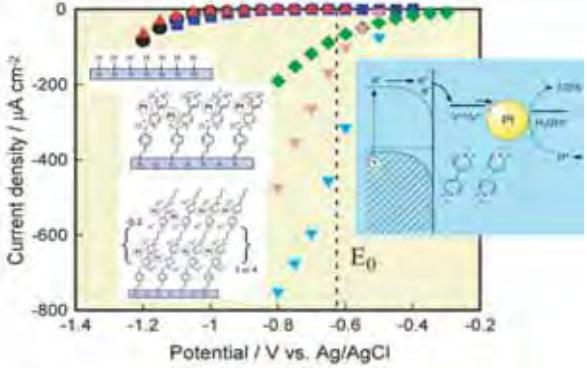


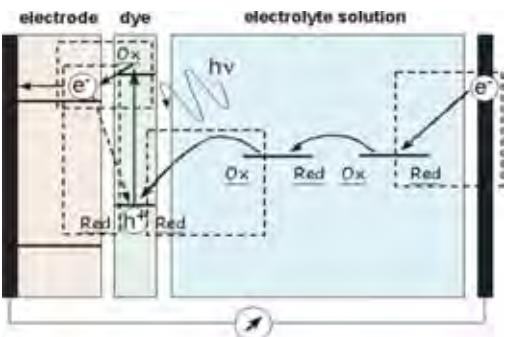
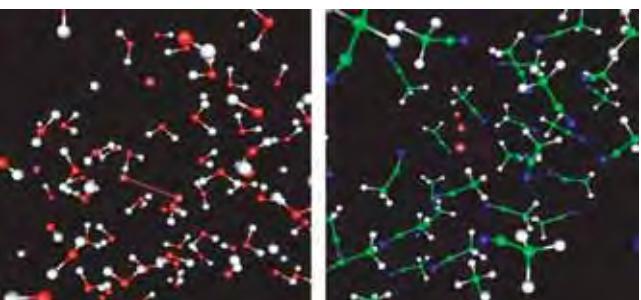
Fig. 2 Schematic illustration of the current increase by the addition of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> colloids.

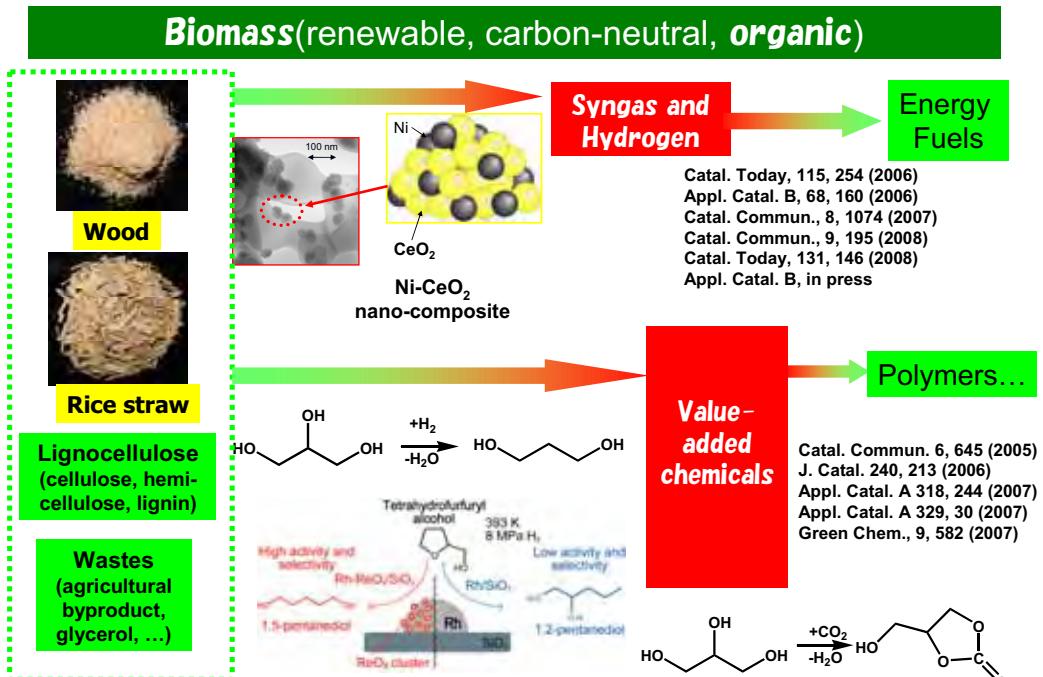
## References:

- (1) R. Nakamura, F. Kai, A. Okamoto, G.J. Newton, K. Hashimoto, *Angew. Chem. Int. Ed.* 2009, 48, 508–511
- (2) R. Nakamura, K. Ishi, K. Hashimoto, *Angew. Chem. Int. Ed.* 2009 (in press)

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<b>Presentation Title:</b> Toward first-principles electrochemistry	
<b>Abstract:</b> Quantum-mechanical simulations based on density-functional theory have become an extremely powerful tool to understand, predict, and design the properties of complex materials or devices. Simulations of many catalytic and electrochemical processes provide nevertheless significant challenges that directly affect our ability to develop from first-principles new materials for energy storage and conversion. In this talk I will discuss three of these key challenges, and our suggested solutions, for electron-transfer processes [1], catalysis at transition-metal complexes [2], and reactions under applied electrochemical potentials [3].	
	
<b>References :</b>	
[1] H.-L. Sit, M. Cococcioni, and N. Marzari, Realistic, quantitative descriptions of electron-transfer reactions: diabatic surfaces from first-principles molecular dynamics, <i>Phys. Rev. Lett.</i> 97, 028303 (2006).	
[2] H. J. Kulik, M. Cococcioni, D. A. Scherlis, and N. Marzari, Density-functional theory in transition-metal chemistry: A self-consistent Hubbard U approach, <i>Phys. Rev. Lett.</i> 97, 103001 (2006).	
[3] I.Dabo, E. Cancès, Y. Li, and N. Marzari, Vibrational Stark effect for CO on platinum electrodes: First-principles simulations of electrochemical systems under applied voltage, <i>Phys. Rev. Lett.</i> , submitted (2008).	

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<b>Presentation Title:</b> Atomic and Molecular Assemblies for Efficient Energy Conversion at Solid/Liquid Interfaces	
<b>Abstract:</b> Development of the efficient system for inter-conversion of light, chemical and electrical energies is the one of the most important global issues in the 21st century. In natural systems, the inter-conversion is achieved based on well ordered arrangement of organic and biological molecules with various functions such as photon absorption, electron relay, and catalyst, i.e., enzyme. On the other hand, inorganic materials are mainly used for energy/materials conversion in modern technology. The efficiency and durability of these systems are still needs to be improved. Here I would like to describe two examples of the construction of interfacial phases for highly efficient energy/materials conversion at solid/liquid interfaces by arranging atoms and molecules with atomic/molecular resolution.	
<b>1. Construction of photoenergy conversion interfaces by molecularly ordered modification of semiconductor surfaces.</b> Hydrogen is the most important clean fuels in the future and production of hydrogen from water by solar energy is required. Photoelectrochemical (PEC) and photocatalytic decomposition of water has been studied for long time. Most serious problem of PEC production of hydrogen from water is that while semiconductor electrodes with small energy gap can absorb large fraction of solar energy but unstable, those with large energy gap are stable but can absorb only small fraction of solar energy. This can be solved by using semiconductor of small gap and separating the reaction site from the surface. Figure 1 shows that hydrogen evolution current flowed at more positive potentials than the reversible potential at a p-Si(111) electrode surface modified with multi-viologen (molecular wire)-Pt nanoclusters (HER catalyst)-layers under illumination. <sup>1</sup> <b>2. Construction of catalytic interfaces by atomically ordered modification of metal surfaces with foreign metals.</b> Atomically arranged nano-composites were constructed first forming multi-nuclear metal complex layers on a substrate followed by their thermal/electrochemical decomposition. Remarkable increase of electrocatalytic activities for hydrogen evolution and methanol oxidation reactions were obtained using Pt-Ru binuclear metal complexes as starting materials. <sup>2</sup>	
	Figure 1. Photocurrent-voltage relations of p-Si(111) electrode modified with various functional layers.
<b>References:</b>	
[1] T. Masuda, K. Shimazu, and K. Uosaki, <i>J. Phys. Chem. C</i> , <b>112</b> , 29, 10923-10930 (2008). [2] H. Uehara, Y. Okawa, Y. Sasaki and K. Uosaki, <i>Chem. Lett.</i> , <b>38</b> , 148-149 (2009).	

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<b>Presentation Title:</b> Ab initio MD study on redox reactions in electrolyte solutions of DSSC	
<b>Abstract:</b> Chemical reactions coupled to electron transfer (ET), so called 'redox reactions', play crucial roles in diverse topics such as battery, fuel cell, catalysis. Fundamental quantities of redox reactions are characterized by free energies, which are mainly governed by structural fluctuations of the target species (solute) and the environment (solvent) as well as the electronic states of frontier orbitals involved in the ET process. Quantitative calculation methods for such processes thus need to take into account the free energies as well as the electronic states. For this purpose, we have recently established <i>ab initio</i> molecular dynamics (MD) methods for redox reactions. The first idea is combining the essence of the Marcus theory for ET [3,4] with <i>ab initio</i> MD technique [1]. The formulation is found quite compatible with density functional theory (DFT). Incorporating constrained MD scheme of Blue-Moon Ensemble, we have extended the method to reactions with bond breaking/formation coupled to ET on the basis of the thermodynamic integration scheme [2]. We have applied these methods to redox reactions associated with triiodide ( $I_3^-$ ) and iodide ( $I^-$ ) ions in typical electrolyte solutions of dye-sensitised solar cell (DSSC). In spite of many applications as electrolyte, the atomistic mechanisms of these iodide redox reactions have not been fully understood due to the complex nature involving multiple electron transfers and bond changes. There are other issues such as the symmetry breaking of $I_3^-$ depending on the solvents. We have calculated free energies and reaction pathways of the elementary redox processes between $I_3^-$ and $I^-$ , and obtained possible scenario why acetonitrile solution gives better performance than water in DSSC. In the talk we also discuss the application to solid/solution interfaces.	
 	
<b>References:</b> [1] Y. Tateyama <i>et al.</i> J. Chem. Phys. <b>122</b> , 234505 (2005). [2] Y. Tateyama <i>et al.</i> J. Chem. Phys. <b>126</b> , 204506 (2007).	

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<b>Presentation Title:</b> Catalytic conversion of biomass to fuels and value-added chemicals	
<p><b>Abstract:</b></p> <p>Utilization of biomass as a renewable raw material will gain importance as a substitute for petroleum for energy production and in the industrial production of chemical substances for sustainability. For the biomass conversion to fuels, development of new catalytic processes with higher efficiency than conventional methods is introduced. It is found that Ni+CeO<sub>2</sub> nano-composite was effective for the steam gasification of biomass (cedar wood) to synthesis gas (the mixture of CO and H<sub>2</sub>), which can be converted to clean liquid fuels such as Fischer-Tropsch oil, methanol and dimethyl ether. Regarding the biomass conversion to value-added chemicals, useful oxygenates will be one of target chemicals derived from biomass because biomass-related raw materials usually high oxygen content. Attempts have been carried out for the production of terminal-diols, which have a linear carbon-carbon chain and carbons at both edges with the OH group have been used as monomers for production of polyesters and polyurethanes.</p>	
<p><b>Catalytic conversion of biomass to fuels and chemicals</b></p>  <p>The flowchart illustrates the catalytic conversion of biomass. On the left, a green box labeled 'Biomass(renewable, carbon-neutral, organic)' contains images of 'Wood' (a tree branch), 'Rice straw', and 'Lignocellulose (cellulose, hemicellulose, lignin)'. A dashed green box labeled 'Wastes (agricultural byproduct, glycerol, ...)' contains a green box labeled 'Lignocellulose (cellulose, hemicellulose, lignin)'. An arrow points from the biomass sources to a central green box labeled 'Syngas and Hydrogen', which then leads to a green box labeled 'Energy Fuels'. Another arrow points from the biomass sources to a red box labeled 'Value-added chemicals', which then leads to a green box labeled 'Polymers...'. The central green box contains a chemical reaction scheme: <chem>HO-CH2-CH(OH)-CH2-OH + H2 -&gt; HO-CH2-CH(OH)-CH2-OH</chem> (with <math>\Delta H = -100 \text{ kJ/mol}</math>), with conditions: 393 K, 8 MPa H<sub>2</sub>. Below this, a diagram shows a Rh/RuO<sub>x</sub>/SiO<sub>2</sub> catalyst on a RuO<sub>x</sub> cluster, with a 1,5-pentanediol molecule reacting to form a tetrahydrofuran alcohol product. The red box contains a chemical reaction scheme: <chem>HO-CH2-CH(OH)-CH2-OH + CO2 -&gt; HO-CH2-CH(OH)-CH2-O-C(=O)-O</chem>, with conditions: 393 K, 8 MPa CO<sub>2</sub>. To the right of the central green box, a list of publications is provided:</p> <ul style="list-style-type: none"> <li>Catal. Today, 115, 254 (2006)</li> <li>Appl. Catal. B, 68, 160 (2006)</li> <li>Catal. Commun., 8, 1074 (2007)</li> <li>Catal. Commun., 9, 195 (2008)</li> <li>Catal. Today, 131, 146 (2008)</li> <li>Appl. Catal. B, in press</li> </ul> <p>Catal. Commun. 6, 645 (2005) J. Catal. 240, 213 (2006) Appl. Catal. A 318, 244 (2007) Appl. Catal. A 329, 30 (2007) Green Chem., 9, 582 (2007)</p>	

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<b>Presentation Title:</b> Highly Efficient Dye-sensitized Solar Cells	
<b>Abstract:</b> <p>Dye-sensitized solar cells (DSCs) have been widely investigated as a next-generation solar cell because of low manufacturing cost. A dye-sensitized solar cell, generally, comprises a nanocrystalline titanium dioxide electrode modified with a dye fabricated on a transparent conducting oxide, a platinum counter electrode, and an electrolyte solution with a dissolved iodide ion/tri-iodide ion redox couple between the electrodes. In this presentation, strategy for improving efficiency of DSCs was reported. Modeling of equivalent circuit of DSCs, the method for improvement of short circuit density (<math>J_{sc}</math>), open circuit voltage and fill factor were investigated. To understand the mechanism of DSC, an internal resistance was studied by the electrochemical impedance spectroscopy and four internal resistance elements were observed. These were assigned to the charge transfer processes at the counter electrode (<math>R_1</math>), the charge transportation at the <math>TiO_2</math>/dye/electrolyte interface (<math>R_2</math>), the diffusion of iodide and triiodide in the electrolyte (<math>R_3</math>), and the sheet resistance of transparent conducting oxide (<math>R_h</math>). An equivalent circuit model<sup>1)</sup> of DSCs is proposed based on these results (Fig. 1). The decrease of the series-internal resistance was studied based on the equivalent circuit of DSCs in order to improve of fill factor. It is found that the series-internal resistance decreases with increase of the roughness factor of the counter electrodes, the decrease of the thickness of the electrolyte layer and the sheet resistance of the transparent conducting oxide. For the purpose of improving <math>J_{sc}</math>, dependence of incident photon to current conversion efficiency (IPCE) spectra on haze of <math>TiO_2</math> film was investigated. IPCE is widely increased with increase of the haze of <math>TiO_2</math> film, especially in infrared region. A cell with the series-internal resistance of <math>1.8 \Omega cm^2</math> and high haze factor was fabricated. Current-voltage characteristics were measured by Research Center for Photovoltaic, National Institute of Advanced Industrial Science and Technology (AIST, Japan) using a metal mask and with an aperture area of <math>0.219 cm^2</math> under standard AM 1.5 sunlight (<math>100.0 mW/cm^2</math>). An overall conversion efficiency of 11.1% was achieved which is the highest confirmed efficiency. Finally I will talk how to further improve the conversion efficiency.</p>	
<b>Reference:</b> 1) L. Han, N. Koide, Y. Chiba and T. Mitate, <i>Appl. Phys. Lett.</i> , 84, 2433 (2004).	

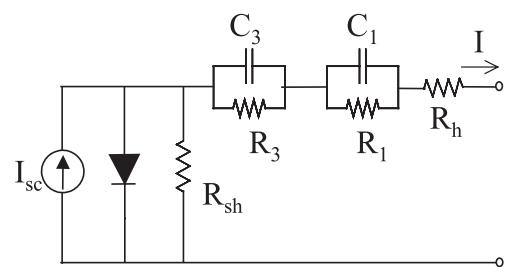
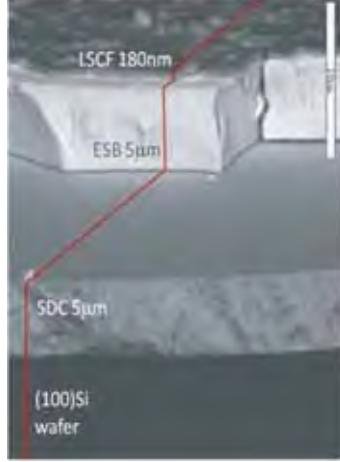


Fig. 1 Equivalent circuit of DSCs.  $R_1$ ,  $R_3$  and  $R_h$  are series resistance elements,  $R_{sh}$  is shunt resistance,  $C_1$  and  $C_3$  are capacitance element.

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<b>Presentation Title:</b> Tailoring Nanostructured Oxide Thin Films for the Miniaturization of Solid Oxide Fuel Cells	
<b>Abstract:</b> The development of micro-solid oxide fuel cells (SOFCs) open new scenarios for portable unit power generation. Micro-SOFCs are likely to produce energy densities per volume and specific energy per weight up to four times larger than state-of-the-art batteries [1]. Reducing the operation temperature is critical for practical use of miniaturized SOFCs and can be achieved using thin-film electrolytes [2]. However, lowering the SOFC operating temperature makes slow the kinetics of charge transfer reactions at the electrolyte-electrode interfaces, mainly at the cathode. This results in a worst fuel cell performance, because the lower the fuel cell working temperature, the larger the cathode overpotential. An increase in their triple phase boundary (TPB) can improve electrode performance.	
Pulsed laser deposition (PLD) is very promising for the fabrication of tailored oxide thin films, because it allows to obtain single crystal or polycrystalline films, with tailored microstructure from dense to highly porous, as we demonstrated in previous works [3]. SOFC components and their assembly, such as dense oxygen ion (ceria), bilayer (ceria/bismuth oxide) and protonic (barium zirconate) electrolyte films in single crystal and polycrystalline forms were fabricated by PLD, with cathode films (LSCF perovskite oxides) deposited on top (Figure 1). Aim of the MANA research project is the fabrication of micro-SOFC devices, starting from the understanding of the nanostructured materials performance as single components (electrolytes) or assembled with the electrodes.	Fig. 1 Tri-layer of LSCF cathode, ESB and SDC electrolyte films, deposited by PLD on (100) Si wafer.
<b>References:</b>	
[1] A. Bieberle-Hüttner et al., J. Power Sources Vol. 177 (2008) 123.	
[2] S.J. Litzelman, J.L. Hertz, W. Jung, H.L. Tuller, Fuel Cells Vol. 5 (2008) 294.	
[3] D. Pergolesi et al, ECS Trans. Vol. 7 [1] (2007) 891.	

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<b>Presentation Title:</b> Design of Nanoarchitected Electrodes for Next-Generation Batteries	
<b>Abstract:</b> Morphology-controlled synthesis of metal nanostructures has attracted considerable interests. It is generally accepted that the morphology (including dimensionality and shape) of the nanostructures can effectively tune their intrinsic chemical and physical properties, <i>e.g.</i> , tailoring the catalytic properties of a functional materials. Up to date, much effort has focused on the development of techniques to produce metal catalysts with a high surface area to achieve high catalytic performance and utilization efficiency. Highly ordered mesoporous (nanoporous) metals with various compositions and morphologies were prepared by finely controlled metallization of metal salts dissolved in aqueous domains of lyotropic liquid crystals. Recently, we have proposed a novel convenient pathway via “Evaporation-mediated Direct Templating” to fabricate mesoporous metals onto several kinds of micro-patterned and micro-fabricated substrates. Various architectures of mesoporous metals with controlled nanostructures should be a key element for creating advanced functional electrode, such as microelectric devices, microchip reactors, miniaturized sensors etc., which will contribute to creation of novel electrochemical catalysts for next-generation batteries. In this paper, I would like to summarize recent advances in the first year of MANA project.	
<b>Selected references in 2008:</b> Yamauchi <i>et al.</i> , <i>Chem. Asian J.</i> , <b>3</b> , 664-676 (2008); <i>J. Am. Chem. Soc.</i> , <b>130</b> , 10165-10170 (2008) (Highlighted in Nature Publishing Group); <i>Adv. Mater.</i> , <b>20</b> , 4728-4733 (2008); <i>Angew. Chem. Int. Ed.</i> , <b>47</b> , 5371-5373 (2008); <i>J. Am. Chem. Soc.</i> , <b>130</b> , 5426-5427 (2008) (Highlighted in Nature Publishing Group); <i>Langmuir</i> , <b>24</b> , 13121-13126 (2008); <i>Chem. Mater.</i> , <b>20</b> , 1004-1011 (2008); <i>Chem. Commun.</i> , 4171-4173 (2008); <i>Chem. Lett.</i> , <b>37</b> , 142-143 (2008); <i>Electrochim. Commun.</i> , <b>10</b> , 681-685 (2008); <i>Chem. Lett.</i> , <b>37</b> , 892-893 (2008); <i>Chem. Lett.</i> , <b>37</b> , 72-73 (2008).	



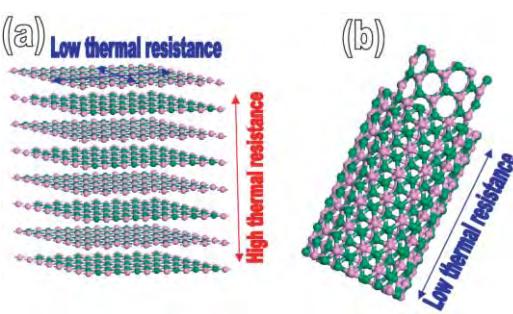
# MANA

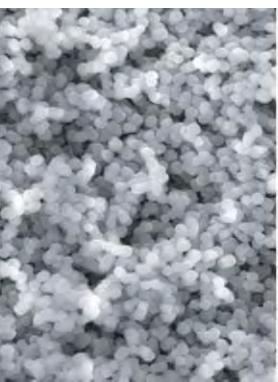
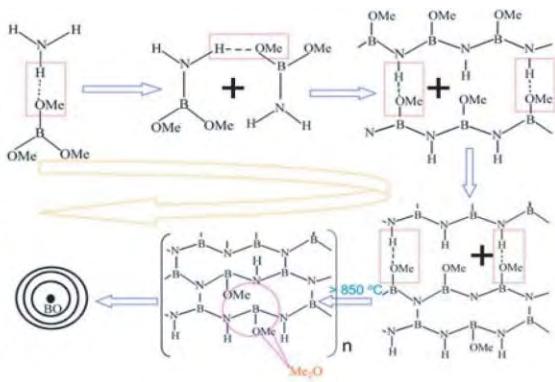
## International Symposium

# 2009

**Poster Session**



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<b>Presentation Title:</b> Towards thermo-conductive electrically insulating polymeric composites using BN nanotubes as fillers																				
<b>Abstract:</b> Boron nitride nanotubes (BNNTs) are electrically insulating counterparts of CNTs due to a constant and wide band gap of ~5.5 eV. Similar to CNTs they possess high thermal conductivity. Theoretical predictions have indicated that the thermal conductivity of a single-walled BNNT may even surpass that of CNT (3000 W/mK). Experimentally, it was found that the thermal conductivity of nanotubes decreased with increasing diameters. The BNNTs with diameters of ~40 nm may have thermal conductivity of 200-300 W/mK along the axis direction, which is notably higher than the numbers for the standard AlN, Al <sub>2</sub> O <sub>3</sub> and BN powders. A principal advantage of one-dimensional nanosize filler utilization can be simply explained as follows. As shown in Figure 1, a conventional BN powder can be considered as a small h-BN crystal which possesses high thermal conductivity in the (002) plane, but a poor thermal transfer along the [002] direction. This gives an overall thermal conductivity of ~30 W/mK even though the thermal conductivity inside the (002) plane can be much higher. However, a BN tubular structure makes it possible to solely utilize high thermal conductivity of the (002) planes while minimizing the effect of other crystal faces especially in well-aligned tubular layers. Moreover, BNNTs are chemical inert, oxidation-proof and structurally stable. These features make a BNNT a highly attractive material for increasing thermal conductivity and reducing CTE of advanced insulating polymers.																				
Utilizing boron nitride nanotubes (BNNTs) as fillers polymethyl methacrylate (PMMA), polystyrene (PS), polyvinyl butyral (PVB) and polyethylene vinyl alcohol (PEVA) composites were fabricated and their thermal, electrical and mechanical properties were evaluated. More than 20-fold thermal conductivity improvement in BNNT-containing polymers was obtained (Table I), and such composites keep good electrical insulation. The coefficient of thermal expansion (CTE) of BNNT loaded polymers was dramatically reduced due to interactions between polymer chains and the nanotubes. Moreover, the composites possess good mechanical properties, as revealed by micro-Vickers hardness tests. This detailed study indicates that BNNTs are very promising nanofillers for polymeric composites which allow one to simultaneously achieve high thermal conductivity, low CTE and high electrical resistance required for novel and efficient heat releasing materials.																				
	Table I. Thermal conductivity values of PVB, PS, PMMA, PEVA and their BNNT-containing composites.																			
<table border="1"> <thead> <tr> <th>Thermal conductivity</th> <th>Pure polymer (W/mK)</th> <th>Polymer-BNNTs composites (W/mK)</th> <th>Improvement (multiple)</th> </tr> </thead> <tbody> <tr> <td>PVB</td> <td>0.24±0.03</td> <td>1.81±0.08</td> <td>7.5</td> </tr> <tr> <td>PS</td> <td>0.18±0.01</td> <td>3.61±0.21</td> <td>20.1</td> </tr> <tr> <td>PMMA</td> <td>0.15±0.03</td> <td>3.16±0.26</td> <td>21.1</td> </tr> <tr> <td>PEVA</td> <td>0.17±0.04</td> <td>2.50±0.05</td> <td>14.7</td> </tr> </tbody> </table>	Thermal conductivity	Pure polymer (W/mK)	Polymer-BNNTs composites (W/mK)	Improvement (multiple)	PVB	0.24±0.03	1.81±0.08	7.5	PS	0.18±0.01	3.61±0.21	20.1	PMMA	0.15±0.03	3.16±0.26	21.1	PEVA	0.17±0.04	2.50±0.05	14.7
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1. C. Y. Zhi, Y. Bando et al, J. Mater. Chem. 18, 3900 (2008) 2. C. Y. Zhi, Y. Bando et al, Adv. Func. Mater. In press (2009)																				

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<b>Presentation Title:</b> Novel Concept for Formation of Boron Nitride Nanoparticles	
<p><b>Abstract:</b>            An intrinsic impetus for the synthesis and characterization of BN nanoparticles is to pursue the potential for improving traditional BN-based composite, taking advantage of the expected excellent thermal and mechanical properties that result from nanoscale effect. However, the number of methods available to produce basic BN nanoparticles in sufficient quantities and impurity-free is limited to say the least. Although the great number of methods for the formation of BN crystal or amorphous have reported in detail, the use of a relatively complicated route and a toxic atmosphere limit their extensive use, even on laboratory scale. For the nanoparticles, there has not been any method already reported and discussed.         </p> <p>The technique reported here represents a continuous process with a low-cost, high-purity and high-yield product, and is particularly useful for future commercial application. A commercially available trimethoxyborane (<math>B(OMe)_3</math>) was found to be a considerably suitable precursor for the CVD synthesis of BN nanoparticles, for the first time, and after 6-years technique improvement, two products with the different character diameters, were systematically developed and these can be immediately commercialized. The formation mechanism of the spherical BN nanoparticles involve two main issues: (1) the formation of a intermediate phase of <math>B(OMe)_{3-x}H_{3-x}N</math> with a normal single B-N bond length; (2) B-O species in the intermediates as the nucleation centers leading to an isotropic growth. The smart development of the spherical BN nanoparticle syntheses may be a vital step to promote applications of BN materials in fillers and thermal interface materials, considering their remarkable insulating, and Rheological properties.         </p>	
 	<p>Figure 1. SEM image and growth mechanism of BN nanoparticles.</p> <p><b>References:</b></p> <ol style="list-style-type: none"> <li>1. C. C. Tang et al, Chem. Comm. 2002, 2826.</li> <li>2. C. C. Tang et al, Adv. Func. Mater. 18, 2008, 3653.</li> </ol>

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**Presentation Title:**

Compositional design, structural analysis and property studies of one-dimensional (1D) wide band-gap semiconductor nanostructures

**Abstract:**

Here we demonstrate that diverse nanostructures including (needle-like) nanowires, (bicrystalline) nanobelts, nanotubes, nanocones and other novel architectures made of various wide band-gap semiconductors, e.g. GaN, ZnS, AlN, GaP, SiC and so forth can be fabricated through a well-designed and carefully controlled chemical vapor deposition (CVD). The nanostructures growth was promoted by a catalyst particle attached to their tips, and the vapor-liquid-solid (V-L-S) growth mechanism thus became in effect. The size, morphology, crystallinity, phase composition, purity, and properties of the nanomaterials were delicately tuned through an experimental conditions control. Moreover, some complex nanostructures can also be fabricated for specific applications. Analyses of crystallography, phases, and constituents of these novel nanostructures were carried out by means of a 300-kV transmission electron microscope (TEM) equipped with an energy dispersive X-ray spectrometer (EDS) and an electron energy loss (EELS) spectrometer. Optical and electrical measurements on the present nano-semiconductors indicated that they exhibit potential applications in novel nano-optoelectronic devices, field emission transistors (FET) and sensors with a tunable working wavelength, i.e. from ultraviolet (UV) to a visible light.

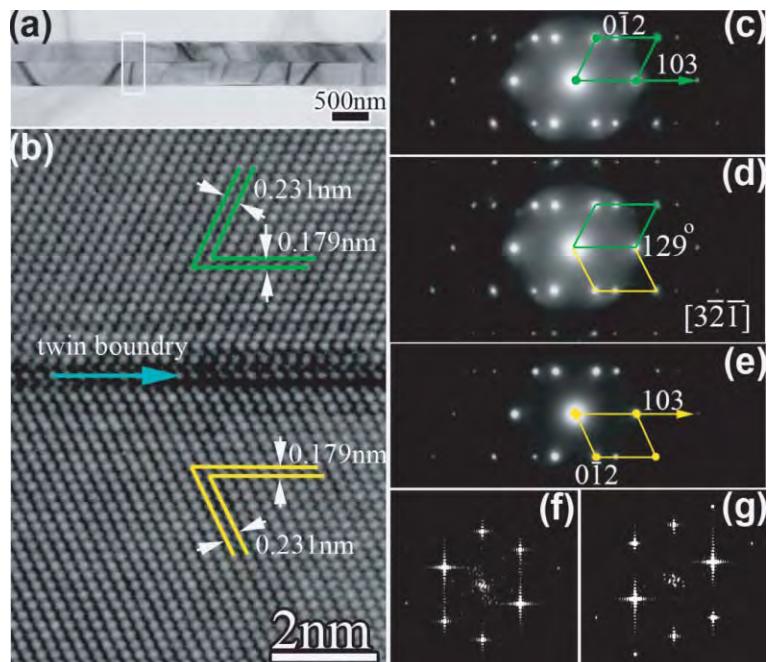
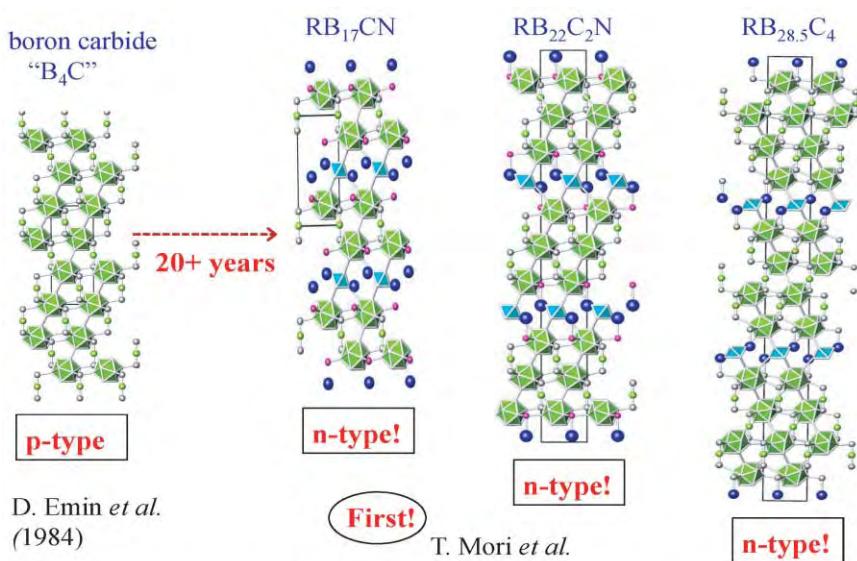


Fig. (a) Low magnification TEM image; (b) HRTEM image and (c) corresponding electron diffraction (ED) patterns of a bicrystalline ZnS nanobelt.

**References:**

[1] B. D. Liu et al, J. Phys. Chem. B, 109, (2005) 10782.

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<b>Presentation Title:</b> Multifunctional Boron Network Compounds as Novel Energy Materials	
<p><b>Abstract:</b></p> <p>Boron is an interesting element, tending to form atomic networks based on clusters and 2D atomic nets in compounds. In this sense it is similar to carbon, which has been much more extensively studied for such materials as fullerenes, nanotubes, and graphite-related materials such as GICs and graphene. A rich vein of materials science potential remains to be tapped and this is illustrated quite well by the recent surprising discoveries of striking phenomena in compounds containing boron.</p> <p>Boron has one less electron than carbon and thus is electron deficient when forming atomic networks, but this causes it to have a special affinity with the rare earth elements and as a result, it forms myriad compounds. This is an excellent combination, because the rare earth atoms supply electrons to the boron atomic framework to stabilize and form novel structures, while the shell of f electrons will supply interesting properties like magnetism.</p> <p>From an application standpoint, the strong covalent boron cluster framework supplies a light robust “armor” which is acid and corrosion resistant and can withstand high temperatures. Attractive electronic, magnetic, and thermal properties can be developed from the inside through metal atom constituents to utilize the protective properties of this network for applications, e.g. discovery of the first n-type boron cluster compound; a possible high temperature thermoelectric counterpart to p-type boron carbide. As an emerging novel phenomenon, it has also been found that a structural building block; the <math>B_{12}</math> icosahedra cluster, is a novel mediator of magnetic interaction.</p> <p>An overview on synthesis methods and physical phenomena is given together with strategies for developing novel and effective thermoelectric materials.</p>	
 <p><b>Fig.1</b> Discovery of long awaited counterpart to boron carbide</p>	
<b>References:</b>	
Takao Mori, “Higher Borides” in <i>Handbook on the Physics and Chemistry of Rare Earths</i> , Vol. 38, ed. K. A. Gschneidner Jr., J. -C. Bünzli, and V. Pecharsky (North-Holland, Amsterdam, 2008) p. 105-173 (2008).	

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**Presentation Title:**

Preparation and photoluminescence characterizations of Ln-photoactivated oxide nanosheets for new phosphor development

**Abstract:**

Nanomaterials have many practical properties for developing phosphor materials. Especially, those with the sheet morphology are suitable for optical device fabrications. We have recently prepared a new kind of nanosheet-based phosphors. These new phosphors consist of transition metal oxide nanosheets as hosts and intrananosheet site Ln (rare earth) ions as photoactivators. The emission wavelength of the Ln photoactivators is characteristic to the f-f transitions of each Ln ion. Thus, phosphors with a desired emission wavelength can be designed utilizing the Ln activators. In addition, the morphology of the nanosheet host can be utilized to effectively absorb excitation energy and to reduce the cross relaxation among the nearby photoactivators. Moreover, by incorporating the Ln activators in intrananosheet sites rather than in internanosheet sites, efficient host-to-activator transfer of excitation energy is expected due to the close interaction between the nanosheet hosts and the activators. The concept of new nanosheet-based phosphor design, and preparation and characterizations of the new nanosheet phosphors will be presented.

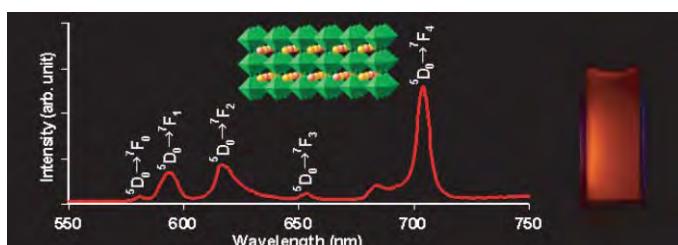
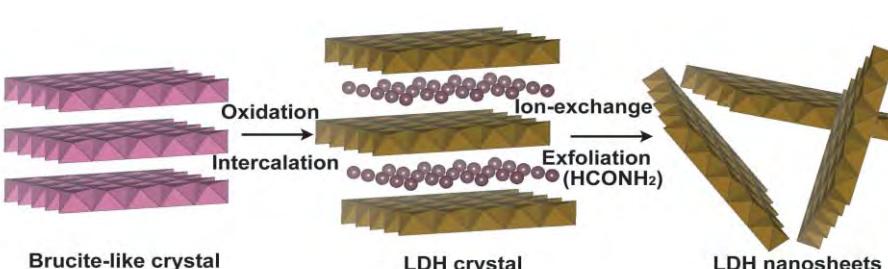
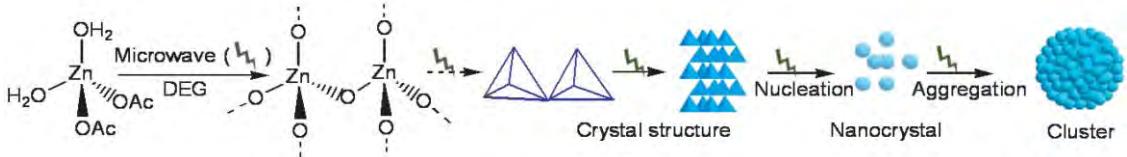


Fig. 1 Photoluminescence emission spectrum and photograph of  $(K_{1.5}Eu_{0.5})Ta_2O_{10}$  nanosheet suspension under UV irradiation.

**References :**

- [1] T. C. Ozawa; K. Fukuda; K. Akatsuka; Y. Ebina; T. Sasaki; *Chem. Mater.*, **19**, (2007) 6575-6580.
- [2] T. C. Ozawa; K. Fukuda; K. Akatsuka; Y. Ebina; T. Sasaki; K. Kurashima; K. Kosuda; *J. Phys. Chem. C.*, **112** (2008) 1312-1315.
- [3] T. C. Ozawa; K. Fukuda; K. Akatsuka; Y. Ebina; T. Sasaki; K. Kurashima; K. Kosuda; *J. Phys. Chem. C.*, **112** (2008) 17115-17120.

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<b>Presentation Title:</b> A Topochemical Approach to Transition-metal Layered Double Hydroxide (LDH) Nanosheets	
<b>Abstract:</b> A topochemical synthetic approach to transition-metal constituting layered double hydroxide (LDH) is described. Uniformly micrometer-sized hexagonal platelets of brucite-type $\text{Co}(\text{OH})_2$ and $\text{Co}_{2/3}\text{Fe}_{1/3}(\text{OH})_2$ were first prepared by a homogeneous precipitation of an aqueous solution containing divalent cobalt and/or ferrous ions through hydrolysis of hexamethylenetetramine (HMT). Subsequent oxidative intercalation processes employing halogens as oxidizing agents transformed them into hydrotalcite-type $\text{Co}^{2+}\text{-Co}^{3+}$ and $\text{Co}^{2+}\text{-Fe}^{3+}$ LDHs, in which the oxidization of a portion of divalent transition-metal cations into trivalent state induced positive charges to the octahedral hydroxyl layers while halide anions were intercalated into the interlayer gallery to balance the extra charge. Due to the topotactic nature of the transformation, resultant $\text{Co}^{2+}\text{-Co}^{3+}$ and $\text{Co}^{2+}\text{-Fe}^{3+}$ LDHs inherited high crystallinity as well as hexagonal platelet morphology from their brucite-type precursors. The topotactic feature was verified by abundant microscopic and spectroscopic characterizations. After a normal ion-exchange process, LDHs intercalating perchlorate anions were exfoliated in formamide into unilamellar nanosheets of $[\text{Co}_{2/3}\text{Co}_{1/3}(\text{OH})_2]^{1/3+}$ and $[\text{Co}_{2/3}\text{Fe}_{1/3}(\text{OH})_2]^{1/3+}$ . These positively charged transition-metal hydroxide nanosheets are ideal building blocks for ultrathin films/coatings, nanocomposites and electromagnetic devices.	
	
Fig. 1 Schematic illustration of topochemical synthesis and exfoliation of transition-metal LDHs.	
<b>References:</b>	
[1] R. Ma, Z. Liu, K. Takada, N. Iyi, Y. Bando, T. Sasaki, <i>J. Am. Chem. Soc.</i> 129 (2007) 5257.	
[2] R. Ma, K. Takada, K. Fukuda, N. Iyi, Y. Bando, T. Sasaki, <i>Angew. Chem. Int. Ed.</i> 47 (2008) 86.	

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<b>Presentation Title:</b> Microwave-Polyol Synthesis of Size-Controlled ZnO Colloidal Nanocrystal Clusters	
<b>Abstract:</b> <p>Over the past decade, formation of monodispersed colloidal nanocrystals with size and shape control has been intensively pursued. This topic is of key importance for elucidating unique size/shape-dependent physiochemical properties and for exciting applications in optoelectronics, sensing, catalysis, crystallization, and mineralization. Currently, a major research direction appears to be shifting to create size and shape-selective secondary structures of colloidal nanocrystals either by self-assembly or through direct solution growth. As expected, manipulation of secondary structures of colloidal nanocrystals leads to fine-tuned interactions between nanocrystal subunits, and eventually enhanced collective properties and functionalities of nanocrystal ensembles. In expanding fundamental exploration in this area, nevertheless, there are still concerns and challenges to chemists and materials scientists in developing efficient and cost-effective synthetic methodologies for creating secondary structures of colloidal nanocrystals. In particular, scale-up production of high-quality colloidal nanocrystals from uniform nucleation and nanocrystal growth will become critical to the realization of advanced nanodevices and many high-end nanotechnological applications. Microwave dielectric heating is becoming an increasingly popular method of heating samples for nanomaterial synthesis. Microwave irradiation is a clean, cheap, and convenient method of heating that often achieves higher yields and shorter reaction time. Microwave irradiation is also unique in providing scaled-up processes without suffering from thermal gradient effects, thus opening up new avenues for potentially large-scale industrial production of high-quality nanomaterials. More importantly, modern microwave systems possess the capabilities of time and temperature programming, allowing fast and easy optimization of experimental factors. This is very beneficial for creating numerous synthetic recipes, preparing high-quality nanomaterials, and scaling up production. Taking ZnO as an example, here we present a rapid and economical route based on an efficient microwave-polyol process to synthesize uniform-sized ZnO colloidal nanocrystal clusters (CNCs).</p>	
 <p>The diagram illustrates the microwave-polyol synthesis of ZnO clusters. It begins with a zinc acetate dihydrate molecule (<math>\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}</math>) in a polyol (DEG). Microwaves (<math>\text{h}\nu</math>) trigger the hydrolysis of zinc acetate to form zinc hydroxide (<math>\text{Zn}(\text{OH})_2</math>). This intermediate then undergoes a series of nucleation and aggregation steps. First, it forms a 'Crystal structure' (represented by a cluster of blue triangles). This structure then undergoes 'Nucleation' (represented by a cluster of blue spheres) and 'Aggregation' (represented by a larger, more complex blue cluster) to finally form a 'Cluster' (represented by a very large, dense blue sphere).</p>	
Fig.1 Schematic representation of ZnO cluster formation	
<b>References:</b> <ul style="list-style-type: none"> <li>[1] X. L. Hu, J. M. Gong, L. Z. Zhang, J. C. Yu, <i>Adv. Mater.</i> <b>2008</b>, <i>20</i>, 4845.</li> <li>[2] X. L. Hu, J. C. Yu, J. M. Gong, Q. Li, G. S. Li, <i>Adv. Mater.</i> <b>2007</b>, <i>19</i>, 2324.</li> <li>[3] X. L. Hu, J. C. Yu, <i>Adv. Funct. Mater.</i> <b>2008</b>, <i>18</i>, 880.</li> </ul>	

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<b>Presentation Title:</b> Fabrication of Selectivity Controllable Gas Sensor Film Composed by Hollow Mesoporous Carbon Capsules	
<b>Abstract:</b> <p>Sensors for various volatile solvents are of increasing significance in daily life to maintain the safety standards and keeping good environment. The efficiency of a sensor evaluates from their selectivity and sensibility to the sensing molecules. To accomplish the selectivity on certain sensing molecules, it always need the adjustment on the structure of the sensor substrate. We have tried to desire a sensor substrate not only with high selectivity and sensibility, but also controllable selectivity. Carbon capsule with mesoporous wall and macroporous core was used for the formation of sensor film into aqueous solution by mixing with different surfactants. With covering surfactant molecules on the surface of the carbon capsules, we can fabricate stable carbon capsule films through layer-by-layer technique. It was shown that anion surfactants covered carbon capsule preferred to form more homogeneous film structures than the cation surfactants. The study on the adsorption properties of the carbon capsule films indicated high sensitivity and selectivity on aromatic solvent (with phenyl group) vapors compared with porous carbon and silica capsule films. It should be due to the dual pores morphology and benzenoid rings in the carbon capsule structure favoring the adsorption of aromatic solvents. In addition, by imprinting certain molecules in the carbon capsule core, we can control the selectivity on gas sorption according to the imprinted molecules. The carbon capsule films were thus shown as smart sensor films with controllable selectivity on gases sorption (Figure 1).</p>	
<b>References:</b> <ol style="list-style-type: none"><li>1. Ariga, K.; Hill, J. P.; Ji, Q. <i>Phys. Chem. Chem. Phys.</i> <b>2007</b>, 9, 2319-2340.</li><li>2. Ariga, K.; Vinu, A.; Ji, Q. M.; Ohmori, O.; Hill, J. P.; Acharya, S.; Koike, J.; Shiratori, S. <i>Angew. Chem. Int. Ed.</i> <b>2008</b>, 47, 7254-7257.</li><li>3. Ji, Q.; Miyahara, M.; Hill, J. P.; Acharya, S.; Vinu, A.; Yoon, S. B.; Yu, J. S.; Sakamoto, K.; Ariga, K. <i>J. Am. Chem. Soc.</i> <b>2008</b>, 130, 2376-2377.</li></ol>	

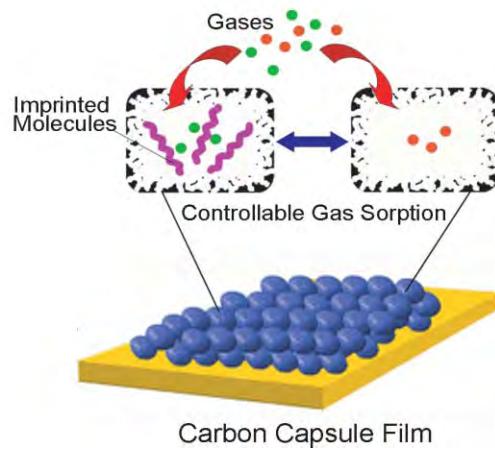


Figure 1. The scheme for carbon capsule film for controllable selectivity on gas sorption.

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Supramolecular Complexes of Oligochromophores with substituted Fullerene

**Abstract:**

Porphyrins and fullerenes are two of the most well studied supramolecular components because of their well defined electrochemical and photophysical properties. Their importance is reinforced by the complementarity of the properties of these two families of compounds, and bolstered by their now well-developed synthetic chemistries. We chose to combine “jaws” porphyrin-type geometry with an electron deficient oxoporphyrinogen, a tetrapyrrolic linking unit.<sup>1,2</sup> Since this linking unit possesses four sites for substitution, two at each face of the tetrapyrrole, two porphyrins may be positioned on each of the opposing faces of the molecule so that two cofacial bisporphyrin interaction sites can be created in orthogonal geometry in the same molecule. The multi-porphyrin hosts, termed “Twisted, Two-faced Porphyrins”, abbreviated as OxP-(MP<sub>x</sub>)<sub>n</sub> where M = 2H or Zn; n = 2 or 4 and x = meta (m) or para (p), and their complexes with a bis-4-pyridyl-substituted fullerene derivative were investigated using spectroscopic, electrochemical and photochemical methods. Dual binding of non-identical guests by the porphyrin hosts was also investigated.

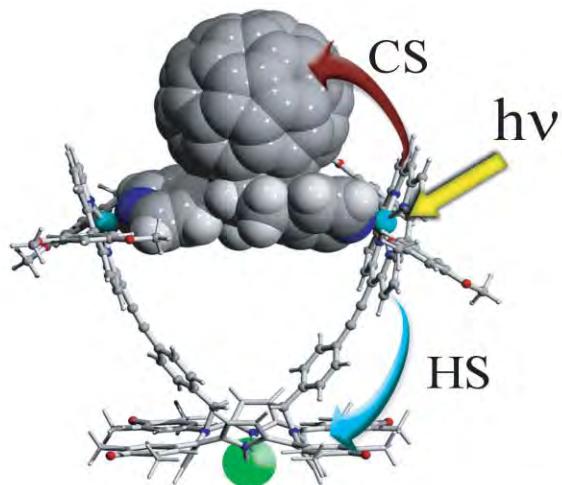
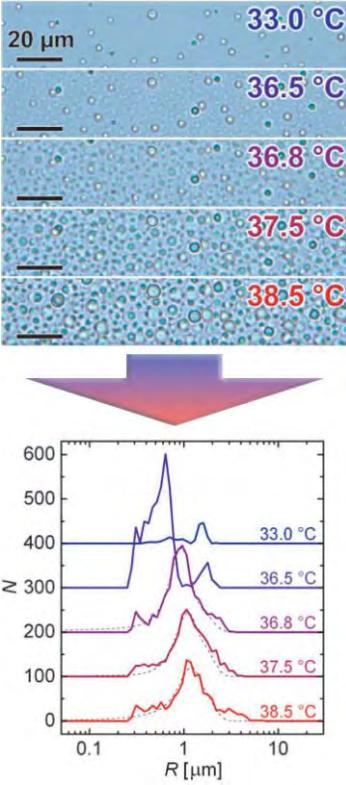


Figure 1. Model of supramolecular oligochromophore complex with fullerene and a second guest

**References:**

1. Hill, J. P.; Sandanayaka, A. S. D.; McCarty, A. L.; Karr, P. A.; Zandler, Charvet, R.; M. E.; Ariga, K.; Araki, Y.; Ito, O.; D'Souza, F. *Eur. J. Org. Chem.* **2006**, 595-603; Schumacher, A. L.; Sandanayaka, A. S. D.; Hill, J. P.; Ariga, K.; Karr, P. A.; Araki, Y.; Ito, O.; D'Souza, F. *Chem. Eur. J.* **2007**, 13, 4628-4635.
2. Xie, Y.; Hill, J. P.; Schumacher, A. L.; Sandanayaka, A. S. D.; Araki, Y.; Karr, P. A.; Labuta, J.; D'Souza, F.; Ito, O.; Anson, C. E.; Powell A. K.; Ariga, K. *J. Phys. Chem. C*, (2008) 112, 10559–10572.

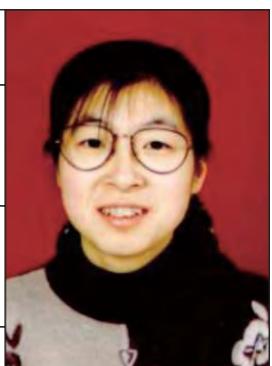
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<b>Presentation Title:</b> Morphological Aspects of Phase Separation in Poly(Vinyl Methyl Ether)/Water/Ethanol Solutions	
<b>Abstract:</b> <p>Poly(vinyl methyl ether) (PVME) exhibits phase separation in water above 308 K as a consequence of a lower critical solution temperature phenomenon (LCST). Such separation is manifestation of a coil-globule transition associated with competition between hydrogen bonding and hydrophobic interactions [1]. We investigated the phase separation of linear PVME in water/ethanol (<math>D_2O/EtOH</math>) mixtures in a broad concentrations range of polymer and ethanol, respectively. The addition of ethanol to aqueous solutions of PVME induces the increase of the LCST. This supports the positive role of ethanol in stabilization of the hydrogen bonds between solvent molecules and PVME.</p> <p>The effect of the polymer and ethanol concentration on appearance and extent of the phase separation was determined from temperature dependences of <math>^1H</math> NMR spectra [2]. Methods of differential scanning calorimetry (DSC), optical microscopy (OM) and dynamic light scattering (DLS) were chosen in order to obtain information regarding reversibility, microscopic morphology and the size of globules during phase separation events. The distribution of the globules' radii at defined temperature was estimated independently by OM (Fig. 1) and DLS measurements.</p>	
<b>References :</b>	<p>[1] Molyneux P., Water-Soluble Synthetic Polymers: Properties and Behavior, Vol. I., Boca Raton (Florida): CRC Press, 1983, 58-61</p> <p>[2] Hanykova L., Labuta J., Spevacek J., <i>Polymer</i> 47, 2006, 6107-6116</p>

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A Convenient Preparation Method for Polymer/Carbon Nanotube Composites with A Core/Shell Structure by In Situ Polymerization Induced by UV Irradiation

**Abstract:**

Since the first report on the preparation of polymer/carbon nanotube(CNT) nanocomposites [1], recently the incorporation of CNTs into polymer matrices has been believed to deliver enhanced functionality and unique properties to the host material [2]. Significant attention has been focused on design and fabrication of CNT/polymer nanocomposites with superior properties, such as high mechanical strength, processability, flexibility, and electric conductivity [3].

Herein we report a convenient preparation method for polymer/multi-wall carbon nanotube (MWNT) composites in the absence of acids from in situ polymerization induced by UV irradiation. The polymer with functionalized side chain can be synthesized by exposing the amine monomer to sunlight. In a similar manner, the polymer/MWNT composites were obtained by simply mixing the amine monomer and MWNTs followed by exposure to natural sunlight. Figure 1 shows the ball structure of prepared polymer. In the obtained polymer/MWNTs, MWNT was trapped by polymer in a core/shell structure, which is shown in Figure 2. Polymer/MWNT composites with different ratios of MWNT were investigated.



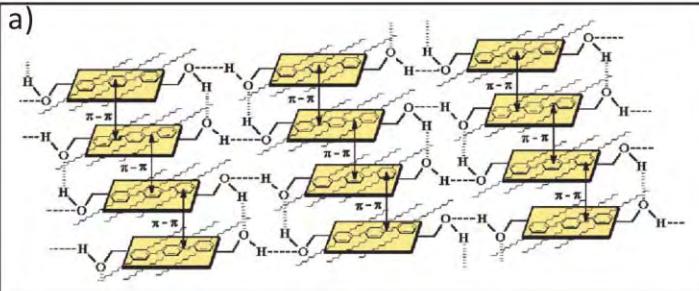
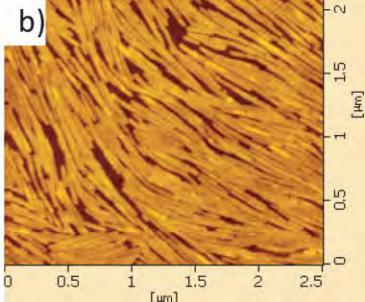
Figure 1. SEM image of polymer.



Figure 2. STEM image of polymer/MWNT composite.

**References:**

1. P. M. Ajayan, O. Stephan, C. Colliex, D. Trauth, *Science*, 1994, **265**, 1212.
2. P. M. Ajayan, J. M. Tour, *Nature*, 2007, **447**, 1066.
3. R. H. Baughman, A. A. Zakhidov, W. A. Heer, *Science*, 2002, **197**, 787.

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<b>Presentation Title:</b> Hierarchical self-assembly of OPV at the air-water interface	
<b>Abstract:</b> <p>Oligo-(paraphenylenevinylene) based molecules equipped with functional moieties which assist in molecular recognition, can self-assemble giving rise to supramolecular architectures with well-defined morphology by means of non-covalent interactions. In this regard it is important to have control over the self-organization process at different levels of hierarchy as the function and the application depends on the level of organization. Extended conjugation in OPVs result in electronic mobility and hence are good candidates for electronic and optoelectronic applications. However the efficiency of many electronic devices based on <math>\pi</math>-conjugated systems depends on the quality, homogeneity and morphology of the thin films. The preparation and study of thin films based on organic materials are of great interest in many science and technology fields. For example, the formation and transfer of well-ordered functional molecules from thin films to solid surfaces, find use in several nanotechnology applications such as molecular sensors, electronic and optoelectronic devices, non-linear optical properties, conducting and semiconductor organic materials.</p>	
 a) Various kinds of interactions possible in OPV, including $\pi-\pi$ stacking, hydrogen bonding, and van der Waals forces.	 b) Uniform fibers of OPV formed at air-water interface, as observed by AFM. The image shows a regular, wavy pattern of fibers with a scale bar of 2.5 $\mu\text{m}$ .
<p>Figure: a) Various kinds of interactions possible in OPV and b) uniform fibers of OPV formed at air-water interface.</p>	
<p>Thin films on flat substrates can be prepared by spin coating technique, but the homogeneity and morphology of such films are usually of low quality. One possible approach towards the preparation of thin films with controlled structure and morphology is the Langmuir-Blodgett technique, which allows to prepare thin films at the air-water interface. In this context we have investigated the self-assembly of OPV molecule at the air-water interface at different conditions and various aspects will be presented.</p>	
<p><b>References:</b></p> <ol style="list-style-type: none"> <li>1. a) F. J. M. Hoeben, P. Jonkheijm, E. W. Meijer, A. P. H. J. Schenning, <i>Chem. Rev.</i> Vol. 105 (2005), 1491-1546; b) A. Ajayaghosh, V. K. Praveen, <i>Acc. Chem. Res.</i> Vol. 40 (2007), 644-656.</li> <li>2. a) K. Ariga, K. Kunitake, <i>Acc. Chem. Res.</i> Vol. 31 (1998), 371-378.</li> </ol>	

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Fabrication of gold nanotape architecture using in-situ generated 1D template

**Abstract:**

Compared with non-dimensional nanoparticles, one-dimensional (1D) nanomaterials are more interesting because of their potential high technological applications for electronics, photonics, nonlinear optoelectronics, waveguide materials and even biomedical applications.<sup>[1]</sup> 1D nanostructures provide a starting point for fabricating future nanodevices with unique properties. Therefore it would be advantageous to assemble the nanoparticles in one-dimensional, where they can communicate to each other very easily. Therefore the requirements of simple and reliable protocols for the synthesis of 1D nanostructure continue to be a major challenge in nanoscience. Over the last few years several research groups have exploited different templates to create metal nanoparticles assemblies.<sup>[2]</sup> However one-dimensional (1D) dense arrays of nanoparticles still remain a great challenge in nanotechnology because it is quite difficult to organize metal nanoparticles in low symmetry; otherwise the metal surface tends to aggregate into two- or three-dimensional structures. In this presentation the formation of 1D dense array of gold nanoparticles has been illustrated. The one-dimensional template is created through specific interaction between gold ions and the chiral surfactant, which favors the formation of a 1D structure in the precursor and these 1D structures are used as template for the fixation of gold nanoparticles without prior functionalization. This novel organic-inorganic hybrid template shows the excellent potential as a nanoreactor for assembly of nanoparticles and their use as a new class of scaffolds for the synthesis of nanomaterials is salient features of the work with implications in crystal engineering and nanocomposites design for various applications.

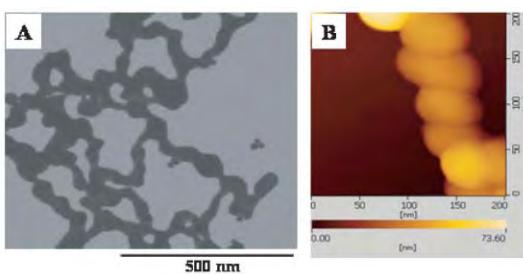
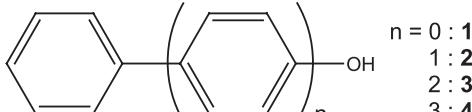
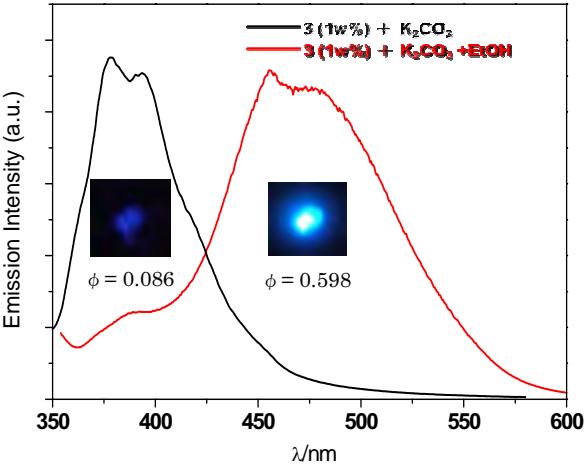
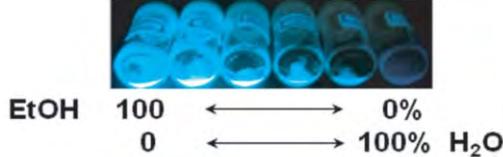


Figure: A and B show the representative TEM and AFM images of nanotapes of 1D assembled gold nanoparticles respectively.

**References :**

- [1] Y. Wu, H. Yan, M. Huang, B. Messer, J.H. Song, P. Yang, *Chem. Eur. J.* **2002**, 8, 1260.
- [2] a) K. J. C. van Bommel, A. Friggeri, S. Shinkai *Angew. Chem. Int. Ed.* **2003**, 42, 980; b) M. Wirtz, C. R. Martin, *Adv. Mater.* **2003**, 15, 455; c) K. Ariga, *J. Nanosci. Nanotechnol.* **2004**, 4, 23; d) A. Sanyal, S. Mandal, M. Sastry, *Adv. Funct. Mater.* **2005**, 15, 273; e) M. G. Warner, J. E. Hutchison, *Nature Mater.* **2003**, 2, 272; f) E. Dujardin, C. Peet, G. Stubbs, J.N. Culver, S. Mann, *Nano Lett.* **2003**, 3, 413.

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<b>Presentation Title:</b> Fluorescence response upon volatile organic solvents to oligo-phenylene phenols	
<b>Abstract:</b> Organic solid-state luminescent materials have been interested in various fields of application. Studies of switching and tuning of solid-state emission properties can be applied to the development of optical sensors and highly luminescent materials for organic light emitting diodes. We introduce aiming at exploring the optical responses of oligo-phenylene phenols towards volatile organic compounds. A series of oligo-phenylene phenols have been synthesized and characterized. Their photophysical and sensing properties towards bases and several organic solvents have been investigated.	
<p>The phenols show a colorimetric response and fluorescence response in the presence of some bases such as DBU, <i>t</i>BuOK, and fluoride ion. When the compound <b>3</b> is blended as a guest in <math>K_2CO_3</math> hybrid matrix, it exhibits rapid and reversible changes in the fluorescence maximum upon drop of several organic solvents.</p> <p>As shown in Fig. 1, the hybrid powder shows weak blue fluorescence in the solid-state. In contrast, dramatically fluorescence change appeared by the addition of a drop of ethanol to the hybrid powder. The fluorescence intensity of the hybrid powder change due to the amount of ethanol (Fig. 2).</p>	 <p>Oligo-phenylene phenol</p> <p><math>n = 0 : 1</math>  <math>1 : 2</math>  <math>2 : 3</math>  <math>3 : 4</math></p>
 <p>Fig. 1. Fluorescence spectra of <b>3</b> and <math>K_2CO_3</math> hybrid powder.</p>	
 <p>Fig. 2. Fluorescence response of <b>3</b> and <math>K_2CO_3</math> hybrid powder in several concentrations of ethanol.</p>	

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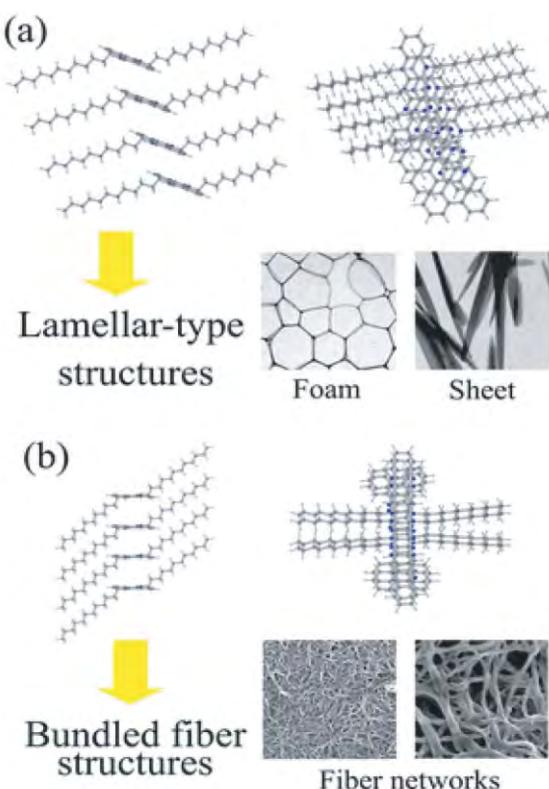
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Towards N-Type Acene Derivatives for Organic Electronic Applications

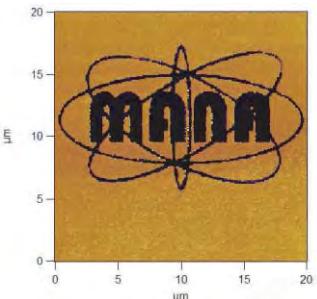
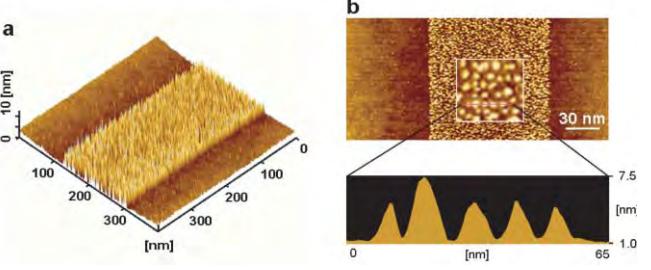
**Abstract:**

There is significant interest in organic semiconducting materials because of their potential application to various developing technologies including organic light-emitting diodes (OLEDs), photovoltaic cells, low-cost integrated circuits, and organic field effect transistors (OFETs). At present, most organic semiconductors, including pentacene, are p-type materials. If plastic electronic devices are to be realised then n-type organic materials will be also a requirement.

We have developed a new synthetic method which allows us to access a series of oligoazaacenes using a simple procedure. *N*-alkylation of the oligoazaacene derivatives gives compounds which can self-assemble to give fiber-like, aggregated plate or membranous bubble architectures.

**References:**

1. Diverse Self Assembly in Soluble Oligoazaacenes; Gary J. Richards, Jonathan P. Hill, Ken Okamoto, Atsuomi Shundo, Misaho Akada, Mark R. J. Elsegood, Toshiyuki Mori and Katsuhiko Ariga; *Langmuir*; Submitted.

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<b>Presentation Title:</b> Charged Molecules Manipulation Using Nano-Domain Patterned Ferroelectric Templates	
<b>Abstract:</b> Multi-functional properties of the ferroelectric materials, such as piezoelectric, pyroelectric and photovoltaic effects, are used to control surface potential and charge of the materials through external fields. For this, lithium niobate (LN) and lithium tantalate (LT) single crystalline substrates are grown using a special technique developed in NIMS. Nano-scale domain switching, another technique also developed in NIMS, is employed to pattern the surface properties (Fig.1). The surface potential and charge can be controlled by controlling external fields such as temperature, atmosphere, and UV irradiation based on pyroelectric and photovoltaic effects of ferroelectric materials. In the vicinity of surfaces, polarization charge induced by pyroelectricity and carrier supplied by photovoltaic effect result in a specific adsorption of charged ions, molecules (including designed DNA) and particles in a nanoscale size on patterned domain surfaces (Fig.2). Self-assembled functional nanoparticles on the patterned domain surfaces lead to the applications of unique templates which enable to induce a surface plasmonic resonance (SPR) by controlling the size and distribution of nanoparticles.	
In this research, potentials of such functional templates are explored under the collaboration with Prof. D. Ginger of Department of Chemistry, Prof. J. Li of Department of Mechanical Engineering, and Dr. X. Liu of Department of Materials Science & Engineering in University of Washington.	
	
Fig.1: Domain writing (polarization switching) is performed by a tip-biased lithography using a contact voltage mode. This technology enables nano-scaled rewritable domain patterning with a comparative high speed.	Fig.2: Distribution of Ag particles on the inverted nanodomain surface. TM-AFM surface morphology images show a self-organized deposition of Ag particles on the inverted +Z surface.
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**Presentation Title:**

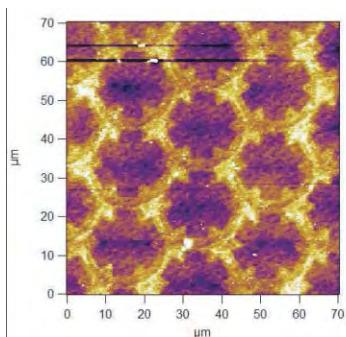
Polymer Blends for Nano-structured Photovoltaic Effect

**Abstract:**

Polymer-based solar cells have the potential for large-scale power generation based on materials that provide the possibility of inexpensive, lightweight, flexible. Since the discovery of the photoinduced electron transfer from a conjugated polymer to fullerene molecules, followed by the introduction of the bulk hetero-junction concept, this material combination has been extensively studied in organic solar cells, leading to several breakthroughs in efficiency, with a power conversion efficiency approaching 5%.

Our research focuses on the physical chemistry of nanostructured materials with potential applications in low cost photovoltaics (solar cells). We study conjugated semiconducting polymer blends such as poly-[2-(3,7-dimethyloctyloxy)-5-methoxy-*p*-phenylenevinylene] (MDMO-PPV), poly-3-hexylthiophene (P3HT), with the fullerene derivative, [6,6]-phenyl-C<sub>61</sub>-butyric acid methyl ester (PCBM). It has been found that the patterned surface chemistry helps greatly to tailor the film morphology of solution-processed donor/acceptor polymer blends on the microscale and nanoscale. We create substrates with patterned monolayers on indium tin oxide (ITO) surfaces using microcontact printing and Dip-Pen Nanolithography (DPN) to pattern functional groups with both micro- and nanoscale features. Spin-coating method is developed to fabricate polymer:PCBM films onto these substrates, followed by thermal annealing under nitrogen, leads to the formation of structured polymer films. Although there are many challenges to develop efficient ordered heterojunctions, it is considered that the most efficient ordered nanostructured polymer device is very significant for enhancing the mobility of polymer solar cell. This program is performed by using SPM technology developed in NIMS under the collaboration with Prof. D.Ginger from Department of Chemistry and Dr. X. Liu from Materials Science & Engineering of UW.

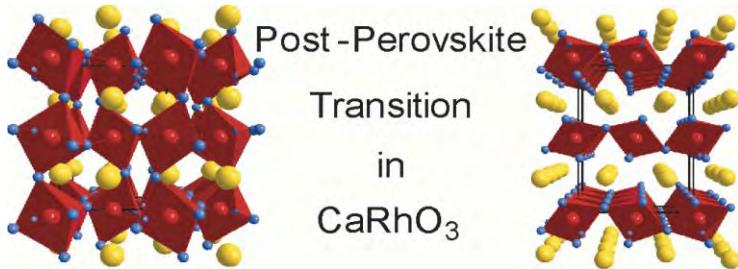
Figures are AFM ac-mode topographic (left) and fluorescence (right) images of P3HT:PCBM films spin-coated on OPA-patterned substrates. Both show a segregation of P3HT-enriched in the dark area, and PCBM-enriched in the bright area.



Film thickness of ~150 nm, excitation at 535-565 nm, emission at 590 nm.

**References:**

A. C. Mayer, S. R. Scully, B. E. Hardin, M. W. Rowell, and M. D. McGehee\*, *Materials Today* 10, 28 (2007).

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<b>Presentation Title:</b> Post-perovskite transition of the correlated 4d oxide CaRhO <sub>3</sub>		
<b>Abstract:</b> <p>Since a post-perovskite transition was discovered in MgSiO<sub>3</sub> in a laser-heated diamond anvil cell, vast attention has been focused on the transition. It likely plays a pivotal role in the cause of D'' seismic discontinuity in the lowermost few hundred km of the earth's mantle. Experimental determination of pressure/temperature variation in the D'' layer is expected to be achieved by further studies of the post-perovskite MgSiO<sub>3</sub>, which may promote understanding of our planet. The post-perovskite is thus believed highly significant in deep earth science; however it is stable only under extreme conditions, higher than 120 GPa/2200 °C, restricting progress of the studies. Besides, the post-perovskite MgSiO<sub>3</sub> is unquenchable, stunting the studies as well. It is, therefore, intensely desired to establish an analogue oxide that is helpful for the studies.</p> <p>In our study, a post-perovskite phase of the correlated 4d oxide CaRhO<sub>3</sub> was attained under a moderate pressure of 6 GPa for the first time [1,2]. Since the post-perovskite is quenchable at ambient pressure/temperature, it can be a valuable analogue of the significant key material MgSiO<sub>3</sub>. The charge transport and magnetic data clearly indicate it goes into an antiferromagnetically ordered state below ~90 K in an unusual way, being a strikingly contrast to what was observed for the metallic perovskite phase. The post-perovskite CaRhO<sub>3</sub> offers future opportunities for correlated electrons science as well as for earth science.</p>		
		
Fig. 1 The perovskite phase (left) and the post-perovskite phase (right) of CaRhO <sub>3</sub> .		
<b>References:</b> <ul style="list-style-type: none"> <li>[1] Y. Shirako <i>et al.</i>, <i>Phys. Chem. Miner.</i> Submitted.</li> <li>[2] K. Yamaura <i>et al.</i>, <i>J. Am. Chem. Soc.</i> in press.</li> </ul>		

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**Presentation Title:**

Superconducting properties of the oxygen-vacant iron oxyarsenide  $TbFeAsO_{1-\delta}$

**Abstract:**

A wide-range doping was attained for  $TbFeAsO_{1-\delta}$  from “under doped” to “over doped” throughout the optimized superconductivity at  $T_c$  of 42 K by controlling the oxygen vacancy concentration,  $\delta$ . A clear bell-shaped feature of  $T_c$  vs.  $\delta$  was observed (see Fig. 1. (d)) similar to the copper oxide superconductors. This similarity between the iron and the copper oxides may imply common physics underlying their superconductivity. The smaller ionic radius of the Tb ion compared with La, Ce, Pr, Nd, Sm ions may play a key role to expand the doping range from the “under-doped” to the “over-doped” region. The maximum doped level chemically available reached 0.5 electrons per f.u. under the present synthesis condition. In the presentation, we will discuss the principal origin of the bell-shaped feature and  $T_c$  reduction in the “over-doped” region. Since a clear “over-doped” superconductivity was observed probably for the first time in the  $LnFeAsO$  system, continuous efforts are directed to investigate nature of the “over-doped” superconductivity. In addition to the  $T_c$  vs.  $\delta$  relation,  $T_c$  vs. lattice constant relation was investigated and it likely follows a unique empirical curve over the whole doping range.

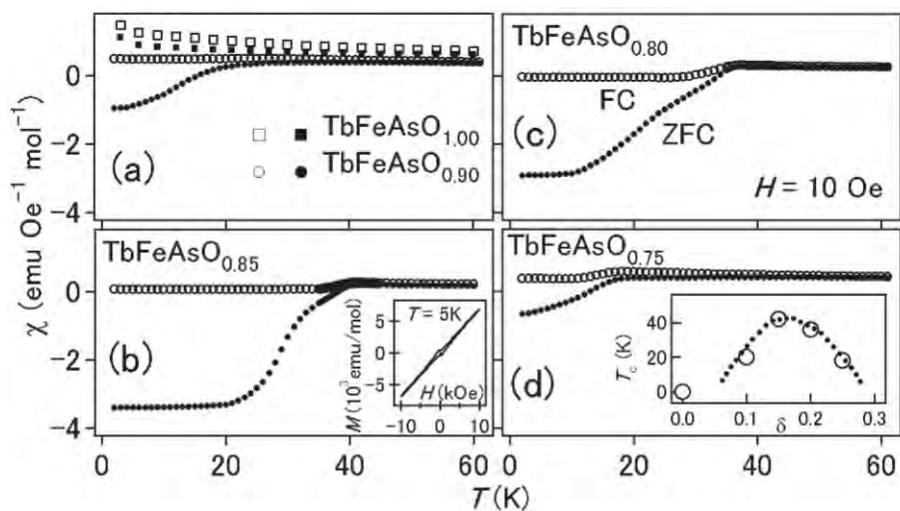


Fig. 1. Oxygen concentration and temperature dependence of dc magnetic susceptibility in the magnetic field of 10 Oe of the polycrystalline  $TbFeAsO_{1-\delta}$ , where (a)  $\delta = 0, 0.1$ , (b) 0.15, (c) 0.2, and (d) 0.25. Insets show (b) the isothermal magnetization curve at 5 K of  $TbFeAsO_{0.85}$ , and (d)  $T_c$  vs.  $\delta$  relation.

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<b>Presentation Title:</b> Formation of crystalline-oriented titania thin films on ITO glass electrodes by electrophoretic deposition in a strong magnetic field	
<b>Abstract:</b> <p>Anatase <math>\text{TiO}_2</math> is a promising candidate for dye-sensitized solar cell (DSSC). In general the photoelectrode of DSSC is composed of stacks of anatase nano particles covered with dye on a conductive glass substrate. Recently, it was reported that some functional properties of anatase such as water reduction and photo oxidation show crystalline-orientation dependence. The photoelectricity conversion behavior of anatase is also expected to depend on the crystalline orientation. Therefore, it is important to develop suitable method to control surface texture. Colloidal processing in a strong magnetic field is an effective method to control the preferred orientation of the crystal faces of deposit layers. The objective of this study is to fabricate textured titania thin films with a thickness of around 10 microns on ITO glass substrates by the electrophoretic deposition (EPD) technique and investigate the influence of the crystalline orientation of the <math>\text{TiO}_2</math> photo-anode on the photo-electrochemical characteristics.</p> <p>Crystal-oriented and crack-free thin <math>\text{TiO}_2</math> films with a good interfacial adhesion on ITO glass substrates for photoelectrode of DSSCs were fabricated by the constant voltage EPD in a strong magnetic field of 12T. A binder-free suspension for the EPD was prepared by dispersing <math>\text{TiO}_2</math> in the mixture of 2-propanol and 2,4-pentanedione (acetylacetone). The electrical conductivity, sedimentation rate and the electrophoretic mobility were measured at varying ratios of the mixed solution to obtain suitable suspension for EPD. The optimized state of the suspension exhibiting the highest surface charge potential and producing deposits with the highest green density was obtained at the 50:50 mixing ratio. The <math>\text{TiO}_2</math> films were characterized by XRD and SEM analyses. It was observed that the photo-current using the films depended on the plane orientation.</p>	
<b>References:</b>	
[1] M. Kawakita, T. Uchikoshi, J. Kawakita, and Y. Sakka: J. Am. Ceram. Soc. accepted for publication. [2] M. Kawakita, J. Kawakita, T. Uchikoshi, and Y. Sakka: J. Mater. Res. accepted for publication.	

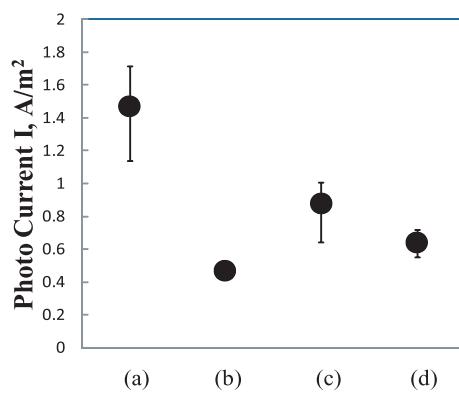
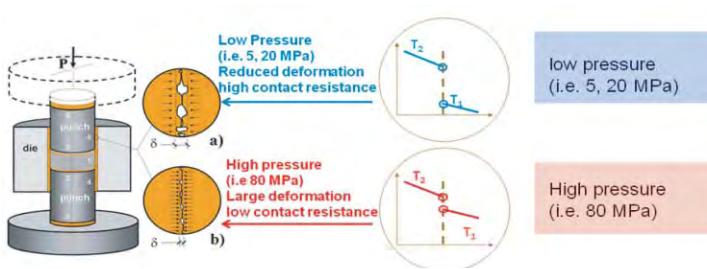


Figure Photo current dependence of oriented  $\text{TiO}_2$  photoelectrodes; (a) c-plane of  $\text{TiO}_2$  parallel to ITO face; (b) preferential-orientation of (101) plane; (c) c-plane of  $\text{TiO}_2$  perpendicular to ITO face; (d) randomly-oriented film.

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<b>Presentation Title:</b> Correlation between applied pressure, homogeneity, properties and microstructure in pure ultrafine WC powder consolidated by Spark Plasma Sintering (SPS)	
<b>Abstract:</b> SPS is a sintering process characterized by an intricate coupled bulk and contact multiphysics, meaning that electric, thermal and stress/strain phenomena are intimately coupled not only within the SPS domain parts (i.e. graphite elements and powder sample) but also along their contact interfaces. In SPS model, the material properties and Joule heat source term are normally assumed as basic coupling factors. Bulk materials properties are assumed to be non linear functions of temperature although, in case of powders, they are also function of the displacement field. Conversely to bulk multiphysics, our understanding on contact multiphysics is more difficult both theoretically and experimentally. The contact pressure plays a crucial role in SPS devices as well. It affects current distribution, both bulk and interface heat generation and heat flow across the contact interfaces. The reason for such behavior was not studied in the details in terms of applied pressure on contact surfaces tightness, lateral deformation - due to uniaxial applied load – and the effect of the initial punch/die clearance [1]. The aim of the present study is to systematically investigate, i.e. with the aid of combined experiments and modeling tools, the influence of applied pressure on horizontal and vertical contact resistances and to correlate pressure effects with radial thermal gradients originating across the punch/compact/sample assembly.	
A combined experimental numerical methodology is developed to fully consolidate pure ultrafine WC powder by means of SPS operating under a current-control mode [2,3]. The investigated applied pressure range from 5 to 80 MPa while the current intensity is held constant to 1400 A. The developed SPS model employs a moving-mesh technique to account for the electro-thermal contact resistance change during shrinkage and punch sliding. The pressure dependence on the electro-thermal contact resistance is also taken into account by the model. The experimental and numerical results clearly show the effects of pressure on the microstructure and hardness along the sample radius. By increasing sintering pressure, complete densification was obtained reducing the peak temperature measured at die surface. By combining experimental and modeling results, a direct correlation among compact microstructure, homogeneity and sintering parameters, such as temperature and applied pressure, can be established.	 <p>Figure 1. Schematics of the punch/die mechanical contact: a) loose contact; b) close contact</p>
<b>References:</b>	
[1] S Grasso, Y Sakka and G Maizza Materials Transactions; 2008, Vol. 49, pp. 2899	
[2] G Maizza, S Grasso and Y Sakka Journal of Materials Science: Accepted for publication on December 09, 2008	
[3] G Maizza, S Grasso, Y Sakka, T Noda and O Ohashi STAM; 2007 Vol. 8 pp 644	

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<b>Presentation Title:</b> A Surface Chemistry Leading to the Unique Optical Properties from Silicon Nanoparticles	
<p><b>Abstract:</b>            The development of highly luminescent materials with emission wavelengths in the range from 300 to 350 nm has attracted tremendous interests in industrial fields for optical applications. Their recent rapid developments have been entirely focused on enhancing the solid-state emitters. Unlike semiconductor compounds, soft-materials, such as organic phosphor molecules, provide many advantages including excellent processability. However, due to limited types of <math>\pi</math>-conjugated molecules and their inherent photoinstability, the development of ultraviolet (UV) emitting soft materials has not been pursued aggressively. Here, we demonstrate a new class of silicon nanoparticle exhibiting an intense PL emission in the ranging from 300 to 350 nm.</p> <p>The synthesis of UV luminescent silicon nanoparticles were respectively performed by (1) the micro-emulsion method and (2) the chemomechanical method with a laser source. In both approaches, the nanoparticles' surfaces were modified with organic monolayers to passivate their surfaces even under ambient conditions. In the former approach, the surfaces of nanoparticles were passivated with alkoxy monolayers. On the other hand, outermost silicon atoms of the nanoparticles synthesized by the latter approach were terminated with alkyl monolayers. Figure 1 shows typical optical absorbance and photoluminescence spectra obtained from alkoxy-terminated silicon nanoparticles. Unlike bulk silicon, the sharp rise in absorption with energies starting at around 4.3 eV gives a well-defined peak centered at 4.9 eV. This strong absorption feature relevant to the direct transition is blueshifted by about 0.4 eV when compared with the bulk, because of the reduction in the nanoparticle size (<math>d \leq 5\text{nm}</math>). The PL spectra of the organic-passivated samples were obtained at room temperature with an excitation wavelength of 266 nm. As shown in the representative spectrum plotted in Figure 1 (solid line), a surprising feature is the appearance of an intense PL emission in the UV wavelength region. Similar optical emission profiles were also observed from the other alkoxy and alkyl terminated nanoparticles. Since the finding of porous silicon in 1990, it has been common knowledge that the effect of quantum confinement imposed upon the charge carriers is postulated to increase the bandgap from 1.1 eV for bulk to <math>\sim 3.0</math> eV for nanoparticles. However, these nanoparticles shows the intense PL emission in the range from 300 to 350 nm. The origin of this unique optical property will be discussed in the presentation of the day.</p>	

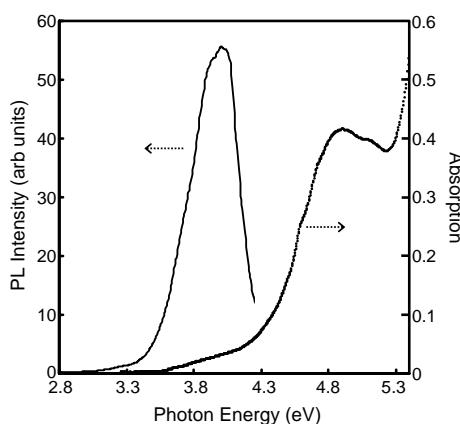
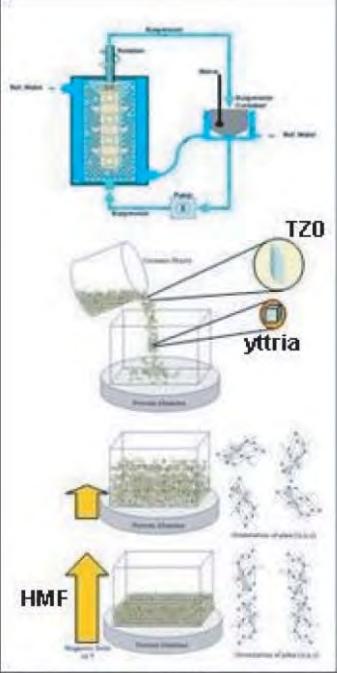


Figure 1. The optical absorbance and photoluminescence spectra for the methoxy passivated nanoparticle. The PL spectrum was collected with an excitation wavelength of 266 nm.

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<b>Presentation Title:</b> Improvements on sintering by optimizing the colloidal processing	
<b>Abstract:</b> Colloidal processing of nano powders is the most important and the initial step in ceramics conformation and it is proved to be the way to control and improve some properties [1]. Ultrasonication treatment is a very useful deagglomeration process however fine particles tend to form heavy agglomeration that can not be re-dispersed.	
The objective of this work is to improve final properties of zirconia designing and controlling the structure by controlling the colloidal processing. “Bead-milling” treatment makes possible full deagglomeration and well-mix of multi-component suspensions using 50 $\mu\text{m}$ beads and high rotation speed.	
We already prove Tetragonal zirconia presents better sinterability if the slip-cast samples are prepared with treated suspensions [2].	
Bead-milling of a mixture 3mol% yttria with 97mol% monoclinic zirconia can produce by reaction sintering an homogeneous nanostructure of tetragonal zirconia sintered by two step sintering presenting a final nanostructure smaller than 3YTZ, 125 nm of average grain size for 3YTZ and 95 nm for reacted sintering. Cubic zirconia can also be prepared by well mix and disperse suspension of 8mol% yttria with 92mol% monoclinic zirconia showing a significant reduction in the grain growth sintered by normal sintering at low temperature, 1300 $^{\circ}\text{C}$ . From a final 1.2 microns for 8YSZ to 250 nm prepared by reacted sintering cubic zirconia.	
Textured materials have shown improvements in many different materials [3]. Tetragonal zirconia is not possible to be oriented in high magnetic field (HMF) unless is prepared by reaction sintering with a bead-mill mixture of yttria and monoclinic zirconia (TZ0) (figure 1).	 <p>The diagram illustrates the experimental setup for bead-milling and slip casting. At the top, a schematic of a bead-milling apparatus shows a central vertical column with a rotating bead mill inside, surrounded by a jacketed vessel. A pump is connected to the bottom of the column. Below this, a sequence of four images shows the process: 1. A beaker containing a greenish suspension with labeled 'TZO' and 'yttria'. 2. The same beaker after being poured into a 'Slip Casting' mold. 3. The mold containing the cast slip. 4. The final textured sample, with an arrow labeled 'HMF' pointing to it, indicating the application of a high magnetic field to the textured sample.</p>
Fabricating zirconia-based composites with CNT is another interesting topic for improving their properties. One of the biggest problems in CNT composites, however, is the dispersion of the CNT in water. Bead-milling can disperse and well mix zirconia with CNT homogeneously making possible the sample preparation with controlled amount of CNT in the matrix.	
<b>References:</b>	
1. Y. Sakka, "Fabrication of Highly Microstructure Controlled Ceramics by Novel Colloidal Processing," <i>J. Ceram. Soc. Japan</i> , 114 371-376 (2006). 2. G. Suárez, Y. Sakka, T. Suzuki, T. Uchikoshi and E. F. Aglietti, "Effect of beads milling treatment in the dispersion of tetragonal zirconia nanopowder and improvements of the two step sintering", <i>in preparation</i> (2009). 3. Y. Sakka and T. S. Suzuki, "Textured development of feeble Magnetic Ceramics by colloidal processing under High Magnetic Field," <i>J. Ceram. Soc. Jpn.</i> , 113 [1] 26 – 36 (2005).	

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**Presentation Title:**  
Electric Properties of Nano-structured Metal Oxides I

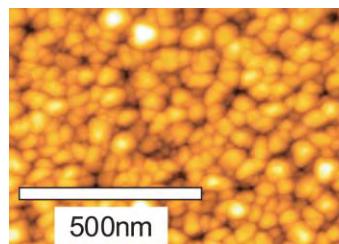
**Abstract:**

Metal oxides, in particular nano-sized ones, exhibit various interesting electronic properties appropriate for sensors and actuators. However, we currently do not have conventional tools for characterization of electronic properties of nano-sized metal oxides, because electric measurements without electrodes are very difficult but the electrodeing to nano-sized structures is expensive. This is one of the bottlenecks for development of nano-sized metal oxides. In the present study, we devoted ourselves to develop methodology for electric characterization of nano-sized structures.

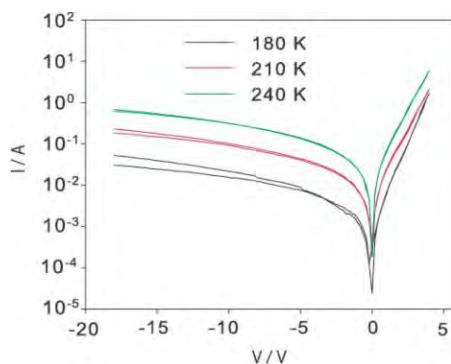
A possible technique is using silicon as a mirror to reflect electric properties of metal oxides. If n-type metal-oxide nano-powder is put on p-type Si, charge transfer between metal oxide and silicon occurs and monitoring this charge transfer phenomena may enable us to see energy dispersion of donors in metal oxides. In this strategy, we investigated electronic measurements for n-(Ti,Sn)O/p-Si hetero-structures to see the potential of this approach for evaluation of electronic properties of metal-oxide nano-powder.

Figure shows typical results of I-V and DLTS measurements for n-SnO<sub>2</sub>/p-Si structure. It has been demonstrated that charge transfer between p-Si and n-SnO<sub>2</sub> nano-powder is evident and characterization of this structure gave information for the electronic structure in nano-sized SnO<sub>2</sub>.

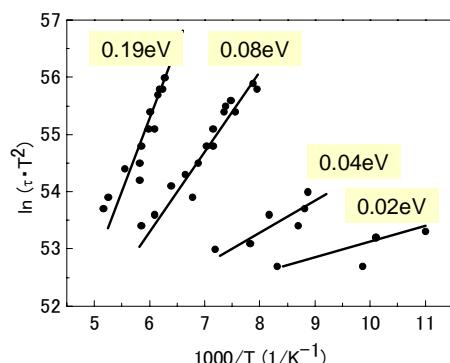
Detailed results will be presented in the conference.



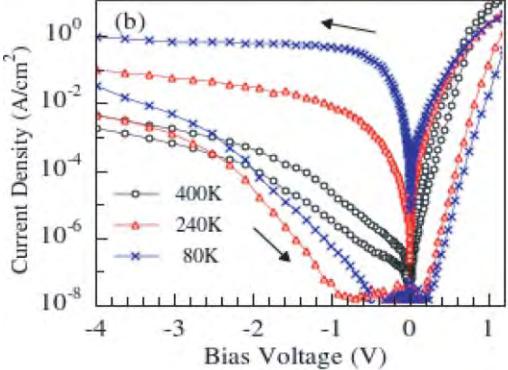
SnO<sub>2</sub> grains on silicon

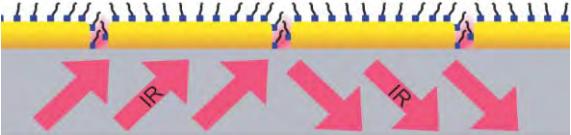
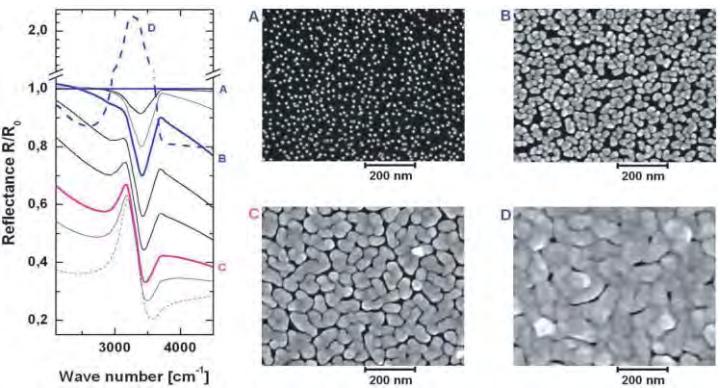


I-V curve for n-SnO<sub>2</sub>/pSi structure



DLTS results for n-SnO<sub>2</sub>/p-Si structure

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<b>Presentation Title:</b> Electric Properties of Nano-structured Metal Oxides II	
<p><b>Abstract:</b>            Perovskite-type oxides possess useful functions such as ferroelectricity. Thus, many investigations on nano-sized perovskite-type metal oxide is currently extensively studied. For developments of nano-sized ferroelectric materials, so-called size-effects, that is suppression of ferroelectricity by reduction of grain size, is one of the crucial issues. Although the size effect has to be considered for developments of micro-devices using ferroelectric metal oxides, there are many difficulties on evaluation of size effects in those materials. Electric field induced property changes in nano-sized metal oxides are also very important issue. If we apply constant bias to a certain material having different size, the filed strength increases proportionally to the inverse material size. In fact, it has been indicated that paraelectric phases transforms to ferroelectric phase by applying very high electric field, and, recently, electric field induced resistance switching is a fascinating topic in terms of non-volatile memory applications. Thus, we have to consider materials size-effect and field strength when we deal with the electric response from nano-sized mater.         </p> <p>In this study, Pt/n-SrTiO<sub>3</sub> interfaces have been investigated to elucidate properties of nano-sized SrTiO<sub>3</sub> under very high field strength. Since the depletion layer width is in nanometric scale in these junctions, the filed strength in for this depletion layer was more than 10MV/m. As seen in the figure, we observed obvious resistance switching behavior at Pt/n-SrTiO<sub>3</sub> junction. From these results, we discuss size effect and field induced property change within the depletion layer having nanometric scale thickness. In fact, we could see huge deviation of electric properties from ordinary Schottky junction model.</p> <p>Detailed results will be presented in the conference.</p>	
 <p>Typical resistance switching behavior observed at Pt/n-SrTiO<sub>3</sub> interface. Here, n-SrTiO<sub>3</sub> was obtained by substituting niobium for titanium.</p>	

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<b>Home Page:</b> n/a	
<b>Presentation Title:</b> Optically monitored wet chemical preparation of plasmonic nanostructures for surface enhanced IR absorption spectroscopy	
<b>Abstract:</b> <p>The effect of Surface Enhanced Infrared Absorption (SEIRA) [1] has become a meaningful tool in chemo- and biosensing. As for the preparation of SEIRA active substrates wet chemical preparation methods have gained much interest in the last years because of their easiness, the low time consumption, and the low cost compared to the known ultra high vacuum based methods. For a routine production of SEIRA substrates, it is necessary to develop not only an easy but also a reproducible procedure of fabrication, to ensure a precise control of the film morphology. Here we demonstrate that optical in situ monitoring of the film preparation process can be of valuable use, utilizing SEIRA of the surrounding molecules as well as the effect of a film morphology dependent shift and change of shape of the surface plasmon absorption band.</p> <p>A two-step wet-chemical preparation method of plasmonic SEIRA active nanostructures for surface enhanced infrared absorption spectroscopy (SEIRAS) is shown. Au nanoparticles are deposited on <math>\text{SiO}_2/\text{Si}</math> and grown to form a network of densely packed tabular islands close to the 2D percolation threshold. In situ IR spectroscopy is utilized to monitor the growth of the Au islands, which enables the termination at a well defined state of the morphology. The SEIRA activity of the resulting films is analysed by measuring IR spectra of octadecanethiol (ODT) monolayers on the respective film. For the antisymmetric <math>\text{CH}_2</math> stretching vibration peak heights of up to 16% were measured, which can be assigned to a SEIRA enhancement of three orders of magnitude compared to flat Au films [2].</p>	 <p>Fig. 1: Detection of adsorbate monolayer on tabular Au islands due to huge enhancement of IR signals in the gaps.</p>
	 <p>Fig. 2: L.s.: In situ IR spectra measured during the Au film formation. R.s.: SEM images of four different Au films corresponding to IR spectra A-D.</p>
<b>Reference :</b>	
[1] A. Hartstein, J. R. Kirtley, and J. C. Tsang, Phys. Rev. Lett. 45, 201 (1980).	
[2] D. Enders, T. Nagao, T. Nakayama, M. Aono, Jpn. J. Appl. Phys. 46, L1222 (2007).	

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Stepwise metal assembling dendrimers and the application to organic electronics devices and atom technology for novel metal oxide materials

**Abstract:**

There has never been nanotechnology to control particle size according to the number of the component. We succeeded the atomic level size-control of  $\text{TiO}_2$  particles (both of rutile and anatase) with a standard deviation of 0.2 nm, using fine controlled metal assembly on a phenylazomethine dendrimer (DPA G4, **Fig. 1A**) [1].

The number and location of the loaded metal ions tend to be random within the previous dendrimers, resulting in a wide distribution of the templated particle in size. However, the number and location of metal ions can be finely controlled in DPA G4 because of the  $\pi$ -conjugated rigid framework. The rigid framework maintains the desirable dendritic and cascade structure [2, 3]. It is reflected on the cascade in the imine basicity on each layer.

The  $\pi$ -conjugated dendrimers with a triphenylamine core are also useful for the application to organic electronics devices, such as organic light emitting diodes (OLED, **Fig. 1B**) and dye-sensitized solar cells (DSSC, **Fig. 1C**). The electron transfer through the  $\pi$ -conjugated framework contributes the control of the electron vector, resulting in higher cell performances [2, 3].

The fine size-control using the dendrimer template on substrate (**Fig. 1D**) revealed the quantum size effect in  $\text{TiO}_2$ . The energy gap of the obtained particles showed a blue shift as decreasing in size and a difference in energy between the anatase and rutile forms. The size-dependency and difference between the crystal forms in bandgap energy is described using a semi-empirical effective mass approximation [1].

**References:**

- [1] N. Satoh, T. Nakashima, K. Kamikura, K. Yamamoto, *Nature Nanotech.*, **3**, 106–111 (2008).
- [2] N. Satoh, J.-S. Cho, M. Higuchi, K. Yamamoto, *J. Am. Chem. Soc.*, **125**, 8104–8105 (2003).
- [3] N. Satoh, T. Nakashima, K. Yamamoto, *J. Am. Chem. Soc.*, **127**, 13030–13038 (2005).

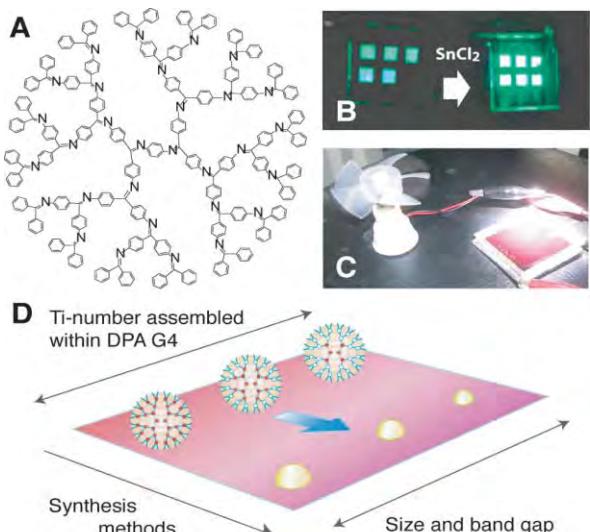


Fig. 1 **A.** Phenylazomethine dendrimer. **B.** OLED. **C.** DSSC. **D.** Scheme of Q-size  $\text{TiO}_2$ .

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Synthesis and Characterization of NIR-Emitting Semiconductor Nanocrystals

**Abstract:**

Luminescent CdSe, CdTe and ternary CdSeTe nanocrystals (quantum dots-QDs), showing tunable luminescence properties from green to near infrared are synthesized by one-step addition of Se, Te or mixture of both ions into the Cd precursor solution at elevated temperature of 300 °C. The resulting nanocrystals reveal very narrow PL emission of about 35 nm at full width at half maximum. By changing the stoichiometry of Se and Te the PL emission of the ternary QDs are tuned from red to NIR region of the wavelength. Transmission Electron Microscope (TEM) equipped with Energy Dispersive X-ray (EDX) module allowed us to characterize the composition of the Qdots. The effect of the composition on optical properties of the nanocrystals will be presented as well. Steady state photoluminescence spectra will be given for each composition under investigation. Typical photoluminescence spectra for ternary CdSeTe are shown in Fig. 1. By increasing the sizes of the QDs the spectra shifts to longer wavelength (lower energies). Fluorescence lifetimes will be presented for the ternary QDs. Photoluminescence excitation spectra of the QDs will be emphasized. The ternary QDs synthesized by us are reproducible and can be used in biosensing, electroluminescent devices, quantum dot-lasers and in optoelectronic devices.

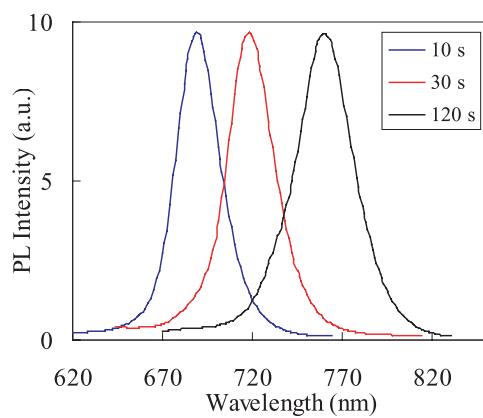
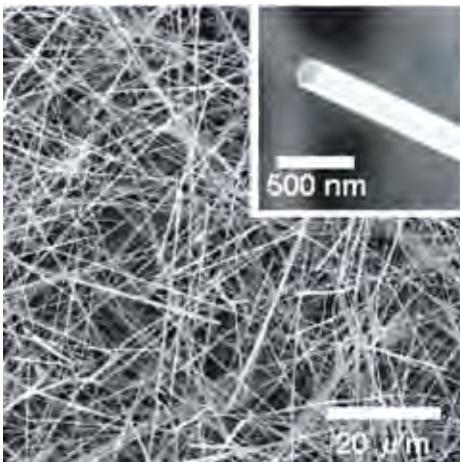
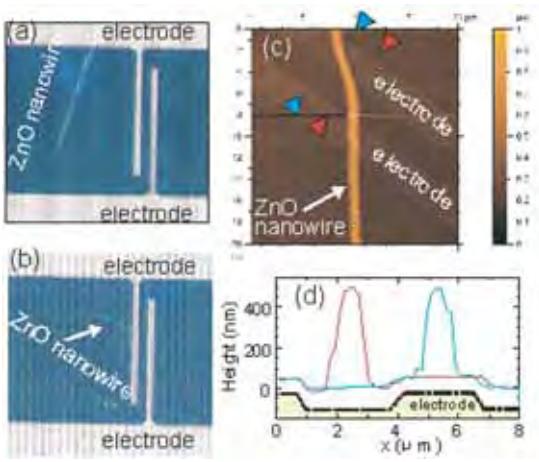
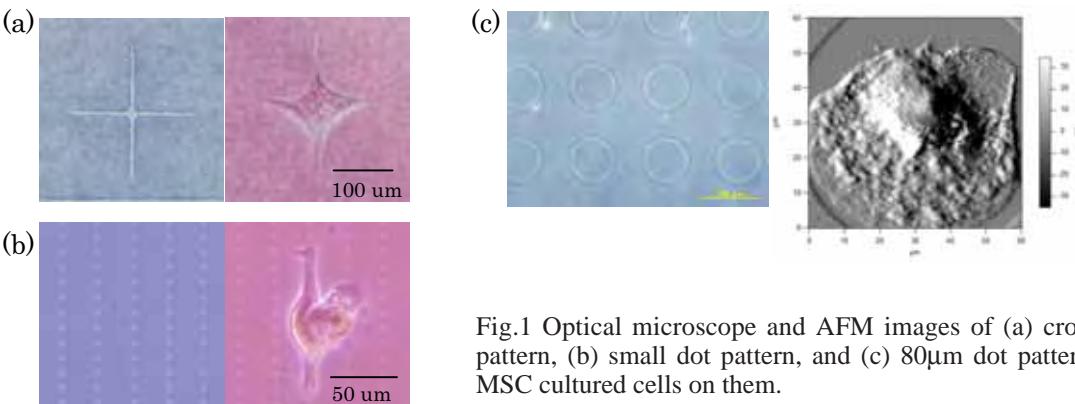


Fig. 1. Emission spectra of ternary CdSeTe QDs.

**References:**

- [1] R. E. Baley, S. Nie, J. Am. Chem. Soc. 125 (2003) 7101.
- [2] E. Jang, S. Jun, L. Pu, Chem. Comm. (2003) 2964.

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<b>Presentation Title:</b> Fabrication and characterization of individual ZnO nanowires	
<p><b>Abstract:</b>            The electrical properties of individual ZnO nanowires were studied using two methods of fabricating junctions between the nanowires and electrodes at room temperature [1]. The first was based on the fabrication of electrodes onto a single nanowire using a lithography technique. ZnO nanowires with metal electrodes had linear <math>I - V</math> curves when carriers were doped by the gate voltage. ZnO nanowires whose carriers were doped by a chemical method demonstrated blue shift in the main peak of the photoluminescence spectra and a linear relation in the <math>I - V</math> curves. The second method involved manipulating the nanowires with AFM onto prepared electrodes (see Fig.2). Ga-doped ZnO electrodes were found to make much better electrical contact with the ZnO nanowires than metal electrodes. The optical properties of the nanowires were measured to understand the behavior of exciton with long life time at room temperature. Based on the experimental results, we discuss about the achievement of novel nanowire network devices.         </p>	
	
<p>Fig.1 SEM image of ZnO nanowires. Inset shows that the nanowire has hexagonal cross-section.</p>	<p>Fig.2 Optical microscope images of ZnO nanowire and metal electrodes taken (a) before and (b) after AFM manipulation. (c) AFM image of ZnO nanowires placed on metal electrode. (d) Cross-sectional line profiles of nanowire and electrodes indicated by red triangles (red curve) and blue triangles (blue curve) in AFM image.</p>
<p><b>References :</b></p> <p>[1] M. Sakurai, YG.Wang and M. Aono, submitted to Nanotechnology</p>	

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<b>Presentation Title:</b> Preparation of cell specimens for nanometrology		
<b>Abstract:</b> <p>Nondestructive and in situ analysis device is required for the measurement of a living cell to investigate its properties, e.g., particular cues for each functionalization and differentiation, as a high-functional elemental device. Simultaneously, understanding how to control the growth and functional aspect of interactions between cells is a significant task in development of future devices such as brain computer, which simulate biosystems. For example, brain neuronal connective networks are implicated to play a variety of roles in the perception, processing and storage of incoming signals. Control over the connectivity within neuronal networks is a promising approach in research on signal transduction by the nervous system. In the field of tissue engineering and cell-based bioassays, surface micropatterning of single or multiple cells is widely used for the spatial control of in vitro cell behaviour, namely, cell adhesion, proliferation, differentiation and signaling pathways. From a material science viewpoint, accurate patterning is achievable by the combination of microfabrication technique (photolithography) with suitable chemical modification.</p> <p>We have taken two approaches to realize in vitro measurements on living cells, development of new probes and preparation of cell specimens. In this presentation, we discuss the latter issue, development of 2D-patterned cell structures using mesenchymal stem cells (MSC) as shown in Figure 1 with an aim to investigate the cell functionalization by shape and spreading control.</p>		
		
<p>Fig.1 Optical microscope and AFM images of (a) cross pattern, (b) small dot pattern, and (c) 80μm dot pattern, MSC cultured cells on them.</p>		

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**Home Page:****Presentation Title:**

Conductive-area-controlled carbon nanotube probes for biological applications

**Abstract:**

Applying multiple-probe scanning probe microscopy to biological systems is an alternative approach for understanding the sophisticated functions of cells. Fig.1 shows an example of such measurement using mesenchymal stem cells (MSC). We fabricated ultra-fine probes applicable to electric measurement in electrolyte for that purpose.

Requirements for such probes are as follows; (1) minimal damage for living cells by probe insertion, (2) nanometer-scale high positioning, (3) nanometer-scale electrically conductive sensing area, and (4) good electrically insulation except for sensing area. To meet these demands, based on the previously developed carbon nanotube (CNT)/Ti probes, we adopted a metal coating for increasing electrical conductivity and insulating materials for electrical insulation. After that, CNT fiber part is cut by focused ion beam technique to fabricate area-controlled nano-electrode. Figure 2 shows an SEM image of an obtained probe. Diameter of the sensing part at the apex of the probe is approximately 100 nm which corresponds to the diameter of metal coated CNT fiber. In this presentation, we discuss the fabrication methods and electrical properties of this probe.

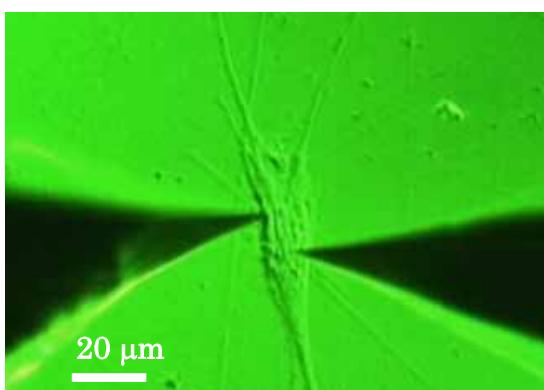


Fig.1 Optical microscope image of demonstration of electric measurement on MSC using nanoscale probes

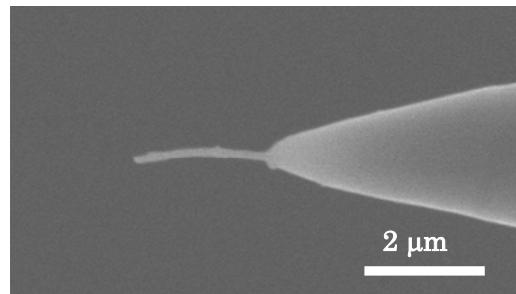
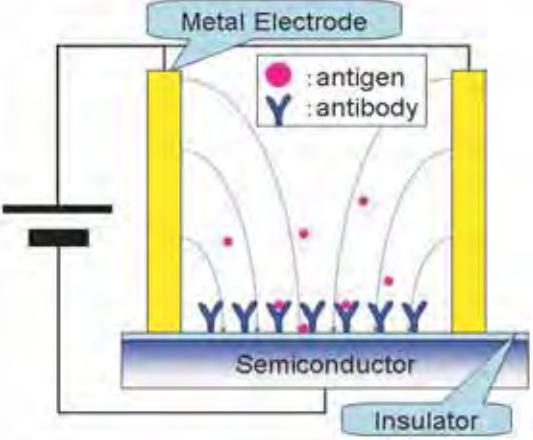
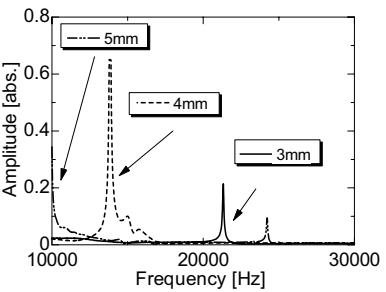
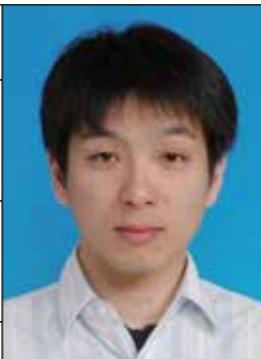
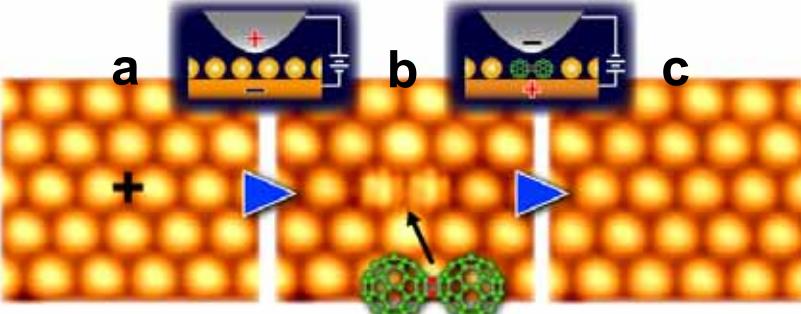


Fig.2 SEM image of fabricated conductive-area-controlled carbon nanotube probe

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<b>Presentation Title:</b> Single molecule SERS with tungsten oxide nanorod Authors: Y. Shingaya, M. Aono, T. Nakayama	
<b>Abstract:</b> <p>We have developed a technique for obtaining extremely large enhancement effect of Raman scattering. Raman scattering from single molecule become detectable. Promising application of this technique is nanoprobe for nanoscale exploration of functionality in biosystems by detecting extremely small amount of molecules, since the technique is based on detection of light and applicable in liquid. Intermediate oxide of tungsten was used as surface enhanced Raman scattering (SERS) active materials. Tungsten oxide nanorods having diameter of 10-100 nm and length of ~10 <math>\mu</math>m were grown on tungsten substrate. Single tungsten oxide nanorod can be transferred to the apex of etched tungsten probe. Figure 1 shows an optical microscope image of a single nanorod on tungsten. SERS spectra were observed by irradiating Laser at the apex of nanorod. The spot size of Laser is about 1 <math>\mu</math>m.</p> <p>Detection of Raman scattering from single or a few molecules was confirmed by observing intensity blinking of Raman scattering. Although as grown nanorod does not have so large enhancement effect, after activation process (slight oxidation of the nanorod), the nanorod gives very large enhancement effect. The activated nanorod was immersed into the 0.1 M NaCl/1nM Rhodamine 6G/water solution. By applying appropriate voltage with electrochemical configuration, blinking of peak of Rhodamine 6G molecule was observed. The blinking was continuously observed for more than one hour. This means the nanorod can be used as very stable SERS active nanostructure in the water.</p>	 Fig. 1 Optical microscope image of $\text{WO}_x$ nanorod attached to the apex of sharpened tungsten. (63 $\mu$ m $\times$ 49 $\mu$ m)

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<b>Presentation Title:</b> MIS-Diode-Typed Reaction Stages for Nano-Bio Interfaces –Detection of Antigen-Antibody Interactions for Tumor Markers	
<b>Abstract:</b> Taking advantage of mass production semiconductor technology for patterning and packaging, a large reaction field (3mm×3mm) for nano-bio-interfaces is constructed on the silicon substrate with line-and-space aluminum working electrodes on the silicon oxide surface. The counter electrode is directly attached to the silicon layer. The device has MIS (Metal-Insulator- Semiconductor) diode structure (see the figure). Dispersion of the electronic characteristics is not observed among the mass-produced chips under low frequencies below 1 kHz. It allows giving a strong and homogenous electric field on the sample molecules located on the silicon surface between the working electrodes. The field strength is roughly determined by the bias voltage divided by the thickness of the silicon oxide, maximally 0.03 V/nm.	
Behaviors of biomaterials under homogenous external fields will be observed in this reaction stage. A biosensing method for immunointeractions is introduced:	
Impedance of PBS (Phosphate Buffered Saline) containing AFP (alpha-fetoprotein) in the reaction field is found to depend on the density of the molecules. Then it is shown that the impedance increases as the AFP density increases under the environment of the anti-AFP antibodies fixed on the substrate while the impedance is nearly constant without the anti-AFP antibodies [1]. It insinuates the antigen-antibody interactions are detected. The sensitivity is comparable to that of the conventional immunoassay such as ELISA.	
Mainly, the resistance and capacitance contribute to the impedance. The reactance, however, is also observed. Large biomolecules seem to conformationally transform under high electric fields.	
<b>References:</b>	
[1] Unpublished report submitted to JST on October 3 <sup>rd</sup> , 2008.	

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<b>Presentation Title:</b> Development of multiple-scanning-probe force microscope	
<p><b>Abstract:</b></p> <p>In order to meet the increasing demands of measuring the physical properties (electrical, optical, magnetic, etc.) of nanoscale objects, multiple-scanning-probe microscopes (MPSPMs) are one of the adequate tools. Taking into consideration the possibility of measuring organic and bio materials, we have developed multiple-scanning-probe tunneling microscope (MPSTM) working in the air with original control software and electronics<sup>[1]</sup>. Not every nanoscale objects (nanostructures, nanodevices, etc.) are conductive, and not every substrate for the nanomaterials are conductive, hence, equipping with the feature of force microscopy is preferable for nanometrology. Consequently, by adopting quartz tuning fork sensors (TF) to the MPSTM system, the multiple-scanning-probe force microscope (MPSFM) is realized without mechanical change nor optical heads. TF with very short tip has been used as a self-sensing probe<sup>[2]</sup> in single probe STM/AFM system. Most commonly, a short tip (&lt; 1 mm) is attached on a prong of the TF perpendicularly or in alignment. However for the MPSPM system, some modifications are needed to move the tips closer to each other in nm order. We therefore optimize the length and angle of tips attached on the TF for MPSFM first. The parallel AFM operation with fine positioning using optimized TF probes will be discussed.</p>	
	
Fig. 1 Example of a resonance curve of optimized TF probes	Fig. 2 Optical microscope image of four TF probes in close-set placement
<p><b>References:</b></p> <p>[1] S.Higuchi, et.al., IEEJ Trans. EIS, Vol.127, No.9, 2007 1314  [2] F.J.Giessibl, Appl. Phys. Lett., Vol. 76 (2000) 1470.</p>	

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<b>Presentation Title:</b> Reversibility-controlled chemical reaction between fullerene molecules and its application for information storage devices	
<b>Abstract:</b> [Masato Nakaya, Masakazu Aono and Tomonobu Nakayama] One of the attractive features of fullerene $C_{60}$ molecules is that their functionality changes depending on intermolecular chemical bonds. Thus, controlling chemical bonds formation (polymerization) and annihilation (depolymerization) between $C_{60}$ molecules at single molecule level is of great interest for realizing nanoscale devices such as a stable switch and nonvolatile memory cells. Here, we present methodology and application of the control of local intermolecular reaction between $C_{60}$ molecules using a tip of scanning tunneling microscope (STM). For experiments, we prepared $C_{60}$ films formed on the highly oriented pyrolytic graphite (HOPG) and on the $Si(111)\sqrt{3}\times\sqrt{3}R30^\circ$ -Ag surfaces. We can control polymerization and depolymerization at room temperature only by selecting an appropriate bias voltage ( $V_s$ ) applied to the $C_{60}$ film. At negative $V_s$ , $C_{60}$ molecules are efficiently reacted with each other via [2+2] cycloaddition reaction beneath the tip (Fig. a-b). In contrast, the created [2+2] cycloadduct tends to dissociate into monomers by applying positive $V_s$ (Fig. b-c). Magnitude of $V_s$ is also important for controlling the spatial precision and the area of the STM-induced chemical reactions. By setting the appropriate polarity and magnitude of the bias voltage, we can induce the polymerization and depolymerization at designated single molecule beneath the tip. We also demonstrate ultradense rewritable data storage into $C_{60}$ films. Writing and erasing of digital data were carried out by inducing polymerization and depolymerization in interlayer of $C_{60}$ multilayer film, respectively, realizing a bit density of 190 Tbits/inch <sup>2</sup> .	
 <p>The figure shows three scanning tunneling microscope (STM) images of a <math>C_{60}</math> film. The background is a regular grid of bright spots representing individual <math>C_{60}</math> molecules.     Image (a) shows the film before polymerization. The molecules are separate and randomly distributed.    Image (b) shows the film after polymerization. The molecules have formed larger, more complex clusters, indicating a polymerized state.    Image (c) shows the film after depolymerization. The molecules have returned to their original, smaller, separate state.    A blue arrow points from (a) to (b), and another blue arrow points from (b) to (c). A black arrow points from the text 'before polymerization' to image (a). A black arrow points from the text 'after depolymerization' to image (c).</p>	
<p>Figure. STM image of <math>C_{60}</math> film <b>a</b> before polymerization, <b>b</b> after polymerization and <b>c</b> after depolymerization</p>	

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<b>Presentation Title:</b> Study of the switching mechanism for $Ta_2O_5$ -based solid electrolyte resistive switch	
<b>Abstract:</b> <p>Resistive switches composed of a solid electrolyte sandwiched between an anode and a cathode have good potential for use as nonvolatile switches and memories in large-scale integrated circuits. Resistive switching has previously been observed mainly for ionic and electronic mixed conductors such as <math>Ag_2S</math> and <math>Cu_2S</math>.<sup>1,2</sup> Recently, another resistive switch, in which <math>Ta_2O_5</math> is used as the solid electrolyte, was demonstrated in order to increase threshold voltages above the operating voltages of complementary metal-oxide-semiconductor devices.<sup>3</sup> However, the switching mechanism of this resistive switch was not fully understood. Here we investigate the electronic transport of <math>Ta_2O_5</math>-based resistive switches with different electrode materials (Cu, Ag, Al, W, Au, and Pt) to reveal the switch mechanism.</p> <p>The switch device consists of cross-point structures with 20-<math>\mu m</math>-wide top (anode) and bottom (cathode) electrodes. A 30-nm-thick <math>Ta_2O_5</math> film was deposited between the two electrodes. Figure 1 shows typical I-V curves of Cu/<math>Ta_2O_5</math>/Pt and Ag/<math>Ta_2O_5</math>/Au structures. It was found that switching occurred at low bias voltages only when Ag and Cu were used as the anode. The I-V measurements for switches with Pt, Au, W, and Al contacts indicated that the bottom interface with Pt and Au is non-ohmic (probably Schottky-like). From AC impedance measurements, we see that the difference in turn-on voltage between two switches of Fig. 1 comes from the difference of conductivity of Cu and Ag ions in the <math>Ta_2O_5</math> film. By combining with these results and the results of Raman scattering measurements, we concluded that Cu and Ag metals precipitate in the <math>Ta_2O_5</math> film, and the switching behavior is determined by the electronic properties of two interfaces with the anode and cathode.</p>	
<b>References:</b> [1] K. Terabe, T. Hasegawa, T. Nakayama, and M. Aono, <i>Nature</i> <b>433</b> (2005) 47. [2] T. Sakamoto <i>et al.</i> , <i>Appl. Phys. Lett.</i> <b>82</b> (2003) 3032. [3] T. Sakamoto <i>et al.</i> , <i>Appl. Phys. Lett.</i> <b>91</b> (2007) 092110.	

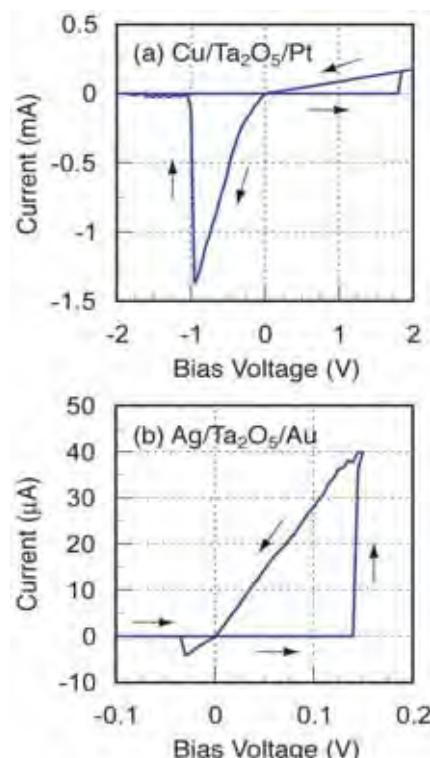


Fig. 1 I-V curves of two switch structures.

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<b>Presentation Title:</b> Synthesis and characterization of ionic conductor nanowires for unique nanoionics devices	
<p><b>Abstract:</b></p> <p>Pure ionic conductor (solid electrolyte) and ion/electron mixed conductor materials have attracted great interest because of their solid electrochemical properties and their device applications such as a fuel cell and a lithium ion battery. Recently, the solid ionics research filed based on a nanotechnology, namely, the nanoionics becomes very hot topics. The nonionics research has possibility to improve the conventional fuel cell and lithium ion battery, further to create the new type of nanodevices that could overcome the limitation of current devices. The nanowire of the ionic conductor is one of promising materials to explore the interesting nanoionics phenomena and create the nanodevice. We found nanostructure of metal chalcogenide based mixed conductor, such as silver sulfide(<math>\text{Ag}_2\text{S}</math>), have shown the great interest as novel nonvolatile nanoswitching.<sup>[1]</sup> In this study, we have electrochemically synthesized the <math>\text{Ag}_2\text{S}</math> nanowire array embedded in a porous alumina template.<sup>[2]</sup> Fig. 1 shows the SEM image of the synthesized <math>\text{Ag}_2\text{S}</math> nanowire after the removal of the alumina template. The nanowire shows the nano-effect on the phase stability. The phase transition point decreases with decreasing the diameter. We also characterized the local structure of the nanowire using SNOM Raman spectroscopy, which reveals the core-shell structures are formed in the <math>\text{Ag}_2\text{S}</math> nanowires embedded in the alumina template. It is found that the nanowire array embedded in the alumina template shows the high ionic conductivity and the resistive switching as shown in Fig.2. The results show the high-density integrated switching could be created using the ionic conductor nanowire array.</p>	
<p><b>References:</b></p> <p>[1] K. Terabe, T. Hasegawa, T. Nakayama, and M. Aono, <i>Nature</i> Vol. 433 (2005) 47  [2] C. H. Liang, K. Terabe, T. Hasegawa, M. Aono, et al, <i>Small</i> Vol. 1 (2005) 971</p>	

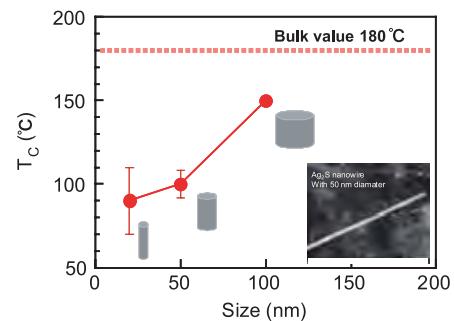


Fig.1 Nano-effect on the phase stability of  $\text{Ag}_2\text{S}$  nanowires and the SEM image of the nanowire.

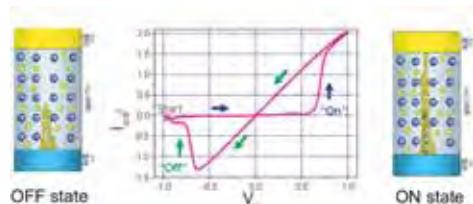
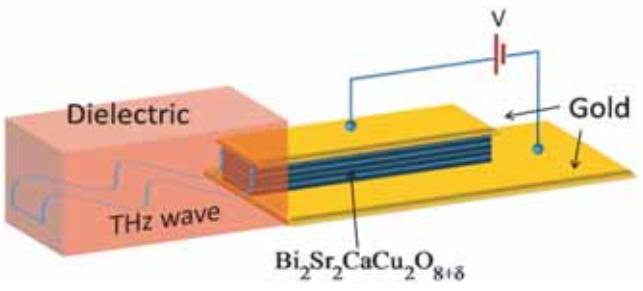


Fig.2 Resistive switching realized by the nanoionics phenomenon in the  $\text{Ag}_2\text{S}$  nanowire.

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<b>Presentation Title:</b> Radiation of Terahertz Electromagnetic Wave from High-T <sub>c</sub> Superconductors	
<b>Abstract:</b> The electromagnetic wave in the terahertz region (0.1THz~10THz) has potential for wide applications, such as cancer detection, security check and so on. However, THz wave is hard to generate either by conventional electronics or by photonics. Thus it is demanding to develop compact, solid-state and cheap generators.	 <p>The diagram illustrates a terahertz wave generator. It features a stack of <math>\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}</math> single crystal layers, which are sandwiched between two gold electrodes. A dc voltage source, labeled 'V', is connected across the gold electrodes. A dielectric block is positioned above the stack, with a 'THz wave' indicated by blue lines emanating from the top surface. The entire assembly is shown in perspective, highlighting the layered structure and the electrical circuit.</p>
	Fig. 1. Schematic view of terahertz wave generator based on high-T <sub>c</sub> superconductors
There are many different techniques to generate THz wave, for instance, quantum cascade laser. Among them, the generator based on intrinsic Josephson junctions in layered high-T <sub>c</sub> superconductors is quite promising since a Josephson junction naturally forms a voltage to frequency converter. The proposed device based on Josephson junctions is sketched in Fig. 1, where a stack of Josephson junctions made of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ single crystal is sandwiched by two gold electrodes and is fed by a dc voltage.	
In 2007, a great breakthrough has been achieved by the joint experimental group from Argonne National Lab and University of Tsukuba, in which continuous and coherent terahertz radiation from BSCCO was clearly observed [1]. It inspired many experimental [2] as well as theoretical efforts [3, 4, 5] to understand and improve the radiation. Using large-scale computer simulations, we found a new dynamic state in layered high-T <sub>c</sub> superconductors, which supports strong terahertz radiation. In this state, large amount of the input dc power is pumped into the plasma oscillation and furthermore, the plasma oscillation is coherent in different junctions. As a result, we have superradiation, which means that the radiation power is proportional to N squared, with N being the number of junctions. The maximum radiation power is about 10mW and the frequency is about 1THz according to our theoretical calculations.	
<b>References:</b>	
[1] L. Ozyuzer <i>et al.</i> , <i>Science</i> <b>318</b> , 1291 (2007). [2] K. Kadowaki <i>et al.</i> , <i>Physica C</i> <b>468</b> , 634 (2008). [3] S.-Z. Lin and X. Hu, <i>Phys. Rev. Lett.</i> <b>100</b> , 247006 (2008). [4] X. Hu and S. -Z. Lin, <i>Phys. Rev. B</i> <b>78</b> , 134510 (2008). [5] S.-Z. Lin and X. Hu, arXiv.0809.5169.	

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Quasiparticles in anisotropic triangular antiferromagnets

**Abstract:**

In usual antiferromagnets without frustrations in dimensions higher than one, spins align antiferromagnetically. However, in the presence of strong frustrations, the antiferromagnetic alignment is no longer stable, and can reduce to a disordered “spin liquid” state. Then, quasiparticles (QPs) different from conventional magnons may emerge. In relation to this issue, the anisotropic triangular antiferromagnet  $\text{Cs}_2\text{CuCl}_4$  has attracted much attention, which exhibits unusual features [1,2] distinct from those of magnons, such as large spectral weights in a wide range of energies in dynamical structure factors and novel incommensurate orders in magnetic fields, which have no classical analogue.

To elucidate QPs responsible for the unusual features, we applied a weak-coupling approach from the one-dimensional (1D) limit, using exact solutions of the 1D chain [3,4]. We found that QPs distinct from magnons and 1D QPs emerge in anisotropic triangular antiferromagnets. The QPs are identified as bound or antibound states of 1D QPs, which do not originate from classical long-range orders. Spectral properties of the QPs well explain unusual features observed in  $\text{Cs}_2\text{CuCl}_4$  in a unified manner as shown in Fig.1.

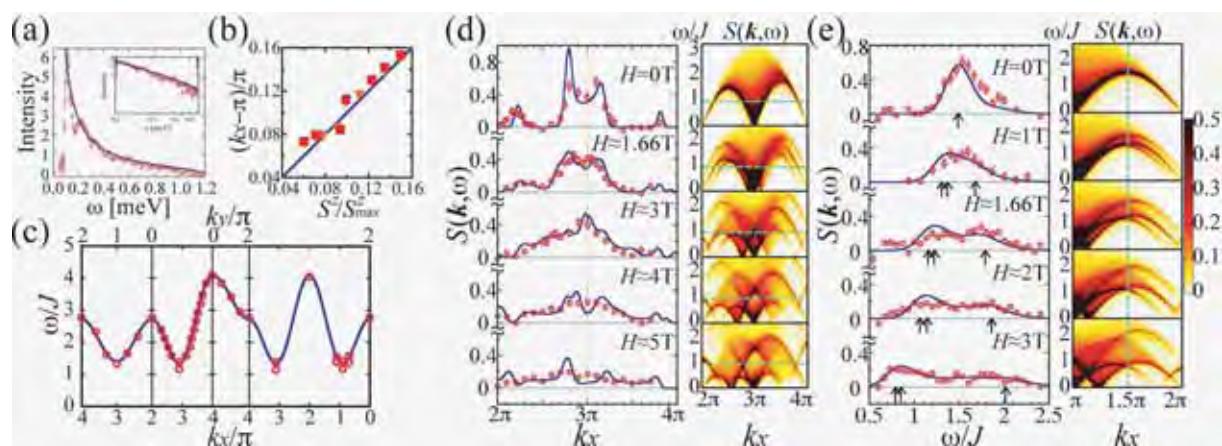
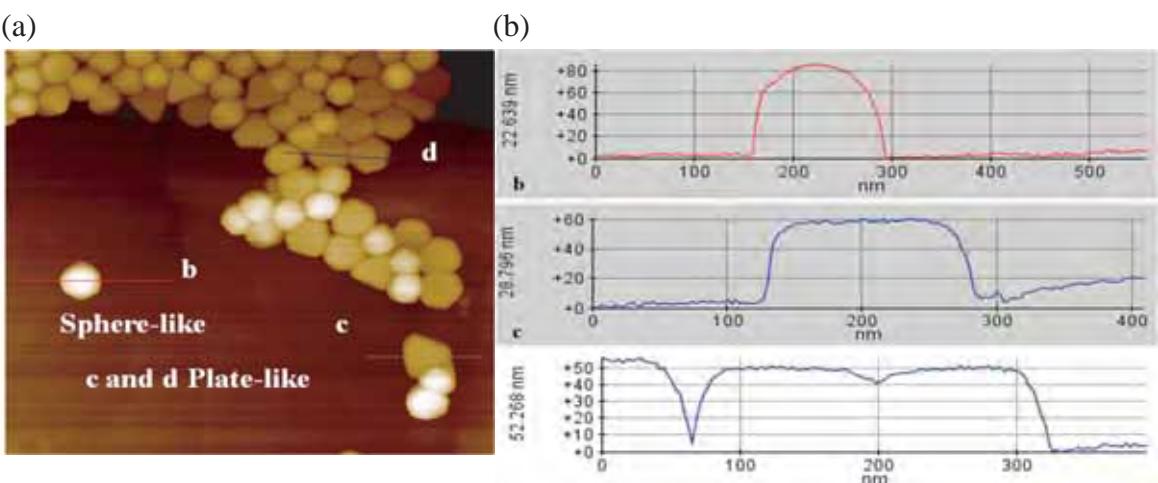


Fig.1 Comparisons with experimental results of  $\text{Cs}_2\text{CuCl}_4$ .  
Solid lines denote present results. Symbols are experimental results.

**References :**

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- [2] R. Coldea *et al.*, Phys. Rev. Lett. **79**, 151 (1997).
- [3] M. Kohno, O.A. Starykh and L. Balents, Nature Phys. **3**, 790 (2007).
- [4] M. Kohno, to appear in Phys. Rev. Lett. (2009).

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<b>Presentation Title:</b> Fabrication and characterization of noble metal nanoparticle structures on the surface of highly ordered pyrolytic graphite wafer	
<b>Abstract:</b> Noble metal nanoparticles such as Au and Ag have received considerable interest in the recent years for various applications, mainly because of their fascinating optical, electronic and catalytic properties (1, 2). In this research, the fabricated noble metal nanoparticles were deposited on a freshly cleaved on highly ordered pyrolytic graphite wafer (HOPG) surface HOPG by a simple solution drop and dried in the air. The as-deposited sample was characterized by use of scanning electron microscope (SEM) along with Auger emission spectroscopy (AES) analysis, atomic force microscope (AFM), Kelvin probe force microscopy (KPFM), scanning tunneling microscope (STM) and Xenon lamp excitation. Fig. 1 shows the typical AFM images of Au nanoparticles on HOPG substrate and corresponding line profiles. The Au particles were distributed on the HOPG surface in the form of single particle, dimer, trimer and multilayer nanostructures etc. The size of Au particle is near homogeneous in the range of ~ 100 nm with three types of shapes, i.e.: sphere, triangle, and hexagonal. These nanostructured Au nanoparticles show fluorescence at ~628 nm when setting the excitation wavelength of Xenon lamp at 600 nm, which is probably ascribed to the interband recombination of electron and hole. The presence of longitudinal surface plasmon resonance is believed to effectively amplify the fluorescence.	
Fig. 1 (a) Typical AFM image, 2μm×2μm; and (b) line profiles of the Au nanoparticles	
<b>Coauthors:</b> D. Fujita, T. Shimada, K. Onishi, M. Kitahara and M. Kitajima	
<b>References:</b>	
1) Bikash Kumar Jena and C. Retna Raj, Chem. Mater. 20(2008) 3546. 2) Kely, K. L., Coronado, E. Zhao L. L., Schatz G.. C., J. Phys. Chem. B 107(2003)668.	

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<b>Presentation Title:</b> Surface compositions and structures on $\alpha$ -phase Cu-9 at. % Al(111) alloy	
<p><b>Abstract:</b>            Copper-aluminum (Cu-Al), a Hume-Rothery alloy, forms an <math>\alpha</math> phase (fcc) of random substitute Al in Cu when the Al composition is below 19.6 at. %. Treating these alloys at elevated temperatures causes strong Al segregation on the (111) face [1]. The segregated Al atoms can form an ordered <math>(\sqrt{3}\times\sqrt{3})R30^\circ</math> superstructure in the top layer of <math>\alpha</math> phase Cu-Al surface [1]. On the other hand, photoemission spectroscopy studies revealed that a Shockley surface state on the (111) face was located at the center of the surface Brillouin zone [2].</p> <p>In this work, Auger electron spectroscopy and low-temperature scanning tunneling microscopy were applied to investigate the surface composition and the electronic structure on Cu-9 at. % Al(111). We found that the amount of Al atoms increased with annealing temperature and time on the surface until it was saturated at <math>\sim 36</math> at. %. This value is slightly higher than but close to the composition of a two-dimensional ordered alloy phase <math>\text{Cu}_{67}\text{Al}_{33}</math> with the <math>(\sqrt{3}\times\sqrt{3})R30^\circ</math> symmetry. The segregating phenomenon of Al atoms on the surfaces was explained well by considering the diffusion length of Al atoms in bulk Cu. Low energy electron diffraction (LEED) measurements showed that the domain size of <math>(\sqrt{3}\times\sqrt{3})R30^\circ</math> structures grew as the concentration of Al atoms increased on the surface. Moreover, our differential conductance images revealed that the standing waves were clearly formed on <math>(1\times 1)</math> and <math>(\sqrt{3}\times\sqrt{3})R30^\circ</math> structures. The Al impurities and dislocations acted as scattering centers to sustain the standing wave formation. By analysis of the <math>\text{dI/dV}</math> images with different bias voltages, a surface electronic feature was observed with significantly downward shifts of the energy levels (Fig. 1). The observed electronic structure showed parabolic energy dispersions of the surface electrons with isotropic effective masses and high electron densities, in strongly contrast with those on pristine Cu(111).</p>	
<p><b>References:</b></p> <ul style="list-style-type: none"> <li>[1] R. J. Baird, T. J. Potter, J. Vac. Sci. Technol. A 3 (1985) 1371.</li> <li>[2] H. Asonen <i>et al.</i>, Phys. Rev. Lett. 46 (1981) 1696.</li> </ul>	

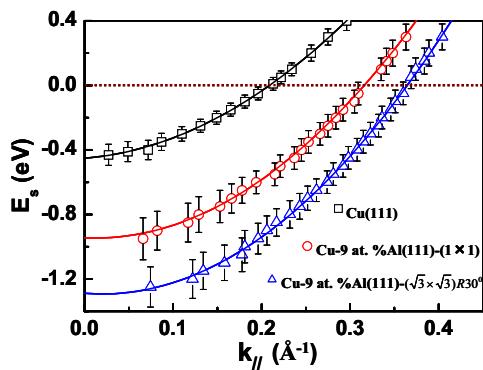
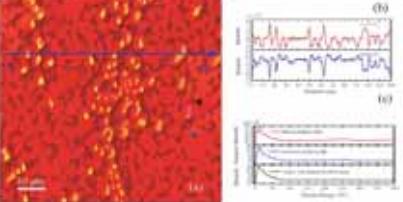
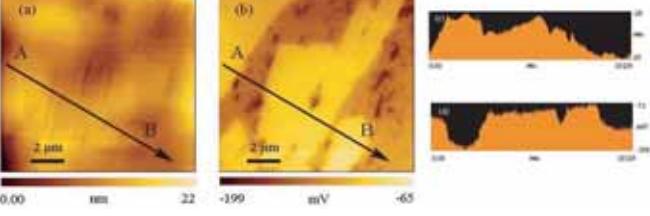
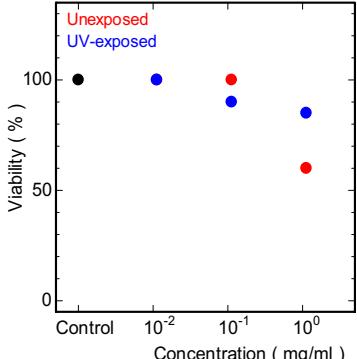
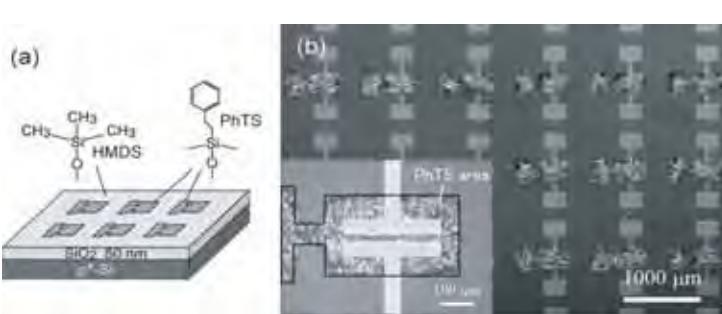


FIG. 1 Energy dispersion of the surface states on Cu(111), Cu- 9 at. % Al(111)-(1x1) and  $(\sqrt{3}\times\sqrt{3})R30^\circ$ .

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<b>Presentation Title:</b> Auger Electron Spectroscopy and Surface Potential of Few Layer Graphene Films Grown on Polycrystalline Metal Surfaces	
<b>Abstract:</b> Carbon-based materials such as carbon nanotubes (CNTs), fullerenes and ultra-thin graphite films, exhibit remarkable electronic properties, and are emerging as ideal candidates for post silicon electronics. Graphene, a honeycomb sheet of one monolayer $sp^2$ bonded carbon atoms, has attracted intense scientific interest, due to high carrier mobility, chemical inertness, and two-dimensional (2D) nature, making it a promising candidate for fundamental research as well as for potential applications in nano-electronics [1-2]. The ultra-thin graphene films were prepared by doping with carbon on polycrystalline Pt-Rh substrates at elevated temperatures. By ultrahigh vacuum Auger electron spectroscopy (UHV-AES) and microscopy measurements, obvious contrast in mapping image (Fig.1(a)) and different characteristics in Auger electron spectrum (Fig.1(b)) can be visible, corresponding to different number of layers for graphene films. Therefore AES measurements can be used as an useful tool to determine the thickness for ultra-thin graphene films. Dynamic Force Microscope (DFM) and Kelvin-probe Force Microscope (KFM) can be used to determine the morphology and contact potential difference (CPD) of graphene films, respectively. From morphology image it is found that the graphene sheets have a height of about 1.0 nm (Fig. 2 (a) and (c)) and from potential image, typical CPD values between graphene film and metal surface vary from about 50mV to 100mV (Fig. 2 (b) and (d)), depending on the thickness of graphene films. By surface potential variation with different film thickness, it is possible to investigate charge transfer mechanism between graphene and metal surfaces.	
	
FIG.1 AES mapping image (a) of graphene ultra-films with kinetic energy 262eV. Line profile (b) of Auger electron intensity for carbon (262eV) and Pt (56eV) from A to B. Carbon Auger spectrum (c) for different coverage with energy from 0 to 400eV.	FIG.2. Topology image (a) and potential image (b) of graphene films on poly crystalline Pt-Rh surfaces. Cross-sectional view of the height (c) and potential (d) variation from A to B.
<b>Co-authors:</b> Daisuke Fujita and MingSheng Xu	
<b>References :</b>	<ol style="list-style-type: none"> <li>1. J. S. Bunch, A. M. van der Zande, S. S. Verbridge, I. W. Frank, D. M. Tanenbaum, J. M. Parpia, H. G. Craighead, and P. L. McEuen, <i>Science</i> 315, 490 (2007).</li> <li>2. H. B. Heersche, P. Jarillo-Herrero, J. B. Oostinga, L. M. K. Vandersypen, and A. F. Morpurgo, <i>Nature</i> 446, 56 (2007).</li> </ol>

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<b>Presentation Title:</b> Silicon nanoparticles as fluorescent labeling of living cells																
<b>Abstract:</b> <p>Fluorescent cadmium-based nanoparticles (NPs) have been developed as bio-imaging material <i>in vitro</i> and/or <i>in vivo</i>. However, concerns have been raised about the toxicological issue of cadmium in biological systems under ultraviolet (UV)-exposure although the material has excellent optical properties, such as size-dependent tunable fluorescence color and high quantum yield of fluorescence for bio-imaging <i>in vivo</i>. Because of the problem, the development of new NPs consisting of non-toxic and more reliable elements is required. Silicon (Si)-NPs are candidate materials for the elimination of any potential toxicology problems. In this study, cytotoxicity of human cervical carcinoma cell line (HeLa) cells labeled with Si-NPs before and after UV-exposure, and the fluorescent imaging of Si-NPs <i>in vivo</i> is discussed. The cytotoxicity examined the viability of HeLa cells having Si-NPs as a function of the concentration using the mitochondrial activity assay. The UV-exposed Si-NPs exhibited a remarkably stable survival curve although the viability decreased only slight with increasing the concentration to 1.12 mg/ml, as shown in Fig. 1. This result substantiated the low toxicity of Si-NPs. Moreover, the fluorescent imaging using Si-NPs was investigated by the circulation from the lymphatic vessel to the lymph node of a mouse. The transfer pathway of Si-NPs could be satisfactorily recognized with the naked eye by detecting the strong red light from Si-NPs, as shown in Fig. 2. Therefore, these features demonstrate the usefulness of Si-NPs as the biological labels for living cell imaging <i>in vitro</i> and/or <i>in vivo</i>.</p>	 <table border="1"> <caption>Data from Figure 1: Viability of HeLa cells</caption> <thead> <tr> <th>Concentration (mg/ml)</th> <th>Unexposed Viability (%)</th> <th>UV-exposed Viability (%)</th> </tr> </thead> <tbody> <tr> <td>Control</td> <td>100</td> <td>100</td> </tr> <tr> <td><math>10^{-2}</math></td> <td>~98</td> <td>100</td> </tr> <tr> <td><math>10^{-1}</math></td> <td>~95</td> <td>~98</td> </tr> <tr> <td><math>10^0</math></td> <td>~80</td> <td>~95</td> </tr> </tbody> </table>	Concentration (mg/ml)	Unexposed Viability (%)	UV-exposed Viability (%)	Control	100	100	$10^{-2}$	~98	100	$10^{-1}$	~95	~98	$10^0$	~80	~95
Concentration (mg/ml)	Unexposed Viability (%)	UV-exposed Viability (%)														
Control	100	100														
$10^{-2}$	~98	100														
$10^{-1}$	~95	~98														
$10^0$	~80	~95														
<b>References:</b>	<p>[1] K. Sato, N. Kishimoto and K. Hirakuri, J. Appl. Phys. Vol.102 (2007) 104305.  [2] K. Sato, N. Kishimoto and K. Hirakuri, J. Nanosci. Nanotechnol. Vol.8 (2008) 374.</p>															

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<b>Presentation Title:</b> Selective molecular assembly for solution-based fabrication of organic field-effect transistors	<b>Abstract:</b> Since the performance of organic field-effect transistors (OFETs) has reached that of amorphous silicon based transistors, practical applications are now being expected. The applications may stem from flexible and light-weight features of organic devices fabricated by a solution or printing technique. We have developed a selective organization technique that allows us simultaneous formation of organic transistor arrays from solution phase. This technique is based on patterned functionalities on surface; difference in wettability given by the surface-modified materials leads the area selective crystallization of soluble organic semiconductors with desired geometry. The self-organized organic films are extended to channels of high performance OFETs. [1].
The self-organized formation of organic layers has been achieved by patterning self-assembled monolayers (SAMs) on the surface of the insulating layer. The insulator surface was coated with a SAM having an alkyl group, providing uniform hydrophobicity over the entire substrate surface. The area that had been selected to be the channel region of the OFETs was then irradiated with ultraviolet light through a shadow mask to remove the alkyl SAM. This area was modified again with a SAM containing a phenyl group. The Phenyl modified surface is wettable for organic semiconductor solutions. As a result, regions are modified to become wettable and unwettable, by Phenyl and alkyl modifications, respectively (Fig. 1(a)). Due to the difference in wettability on the surface, drop-casted organic semiconductor solution is attracted only into the wettable area, which results in organic semiconductor films fully patterned on the insulator. The self-organized organic films are extended to channels of high performance OFETs (Fig. 1(b)).	
	
<p>Fig. 1 (a) Schematic of a silicon dioxide substrate patterned with two SAMs having different wettability for the organic semiconductor solution. (b) Arrays of organic transistors formed by the selective organization technique. Inset shows magnified image of the individual device. Solid line indicates the PhTS-modified area.</p>	
<b>References:</b> T. Minari, M. Kano, T. Miyadera, S. D. Wang, Y. Aoyagi, M. Seto, T. Nemoto, S. Isoda, and K. Tsukagoshi, <i>Applied Physics Letters</i> <b>2008</b> , 92, 173301	

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**Presentation Title:**  
Superconductivity and Magnetic Ordering Induced by Yttrium-doping in  $AFe_2As_2$  ( $A = Sr, Ca$ )

**Abstract:**

Spurred on by the report of higher transition temperatures ( $T_c$ ) in iron oxypnictide,  $LaFeAsO_{1-x}F_x$ , by Kamihara *et al.*,<sup>1</sup> a series of iron-pnictides and iron-chalcogenides has since been discovered to be superconducting some with even higher  $T_c$  compared to the original report. The so-called 122 FeAs compounds ( $AFe_2As_2$ , where  $A = Ba, Sr, Ca, Eu$ ) are the second series in the iron-pnictide family to be synthesized with  $T_c$  reaching up to 38 K.<sup>2</sup> The appealing factor of these ternary iron-arsenides is that all the constituents are metal or semi-metal, which promotes a lower preparation temperature, and their synthesis are more straightforward. Superconductivity in these 122 FeAs can be achieved either through doping with monovalent cations on the alkaline earth metal sites (interlayer hole-doping) or substituting some of the iron with cobalt (intralayer electron doping). This report focuses on work which has been carried out on Sr- and Ca- $Fe_2As_2$  in an attempt to probe whether interlayer electron-doping is possible in these 122 FeAs, with yttrium as the dopant (which ionic radius is in close proximate size to  $Sr^{2+}$  and  $Ca^{2+}$ ). Superconductivity was indeed observed in  $Sr_{1-x}Y_xFe_2As_2$  within a narrow range of  $x = 0.3$  to  $0.5$  (Fig. 1a). Hall effect measurements confirm the electron doping nature of this new superconductor. In  $Ca_{1-x}Y_xFe_2As_2$  despite noticeable diamagnetic signals in the magnetization curves (Fig 1b), superconductivity was not observed in transport measurements, which can only suggest the presence of some interesting magnetic ordering induced by Y-doping, or minute superconducting phases might be included in a large non-superconducting matrix.

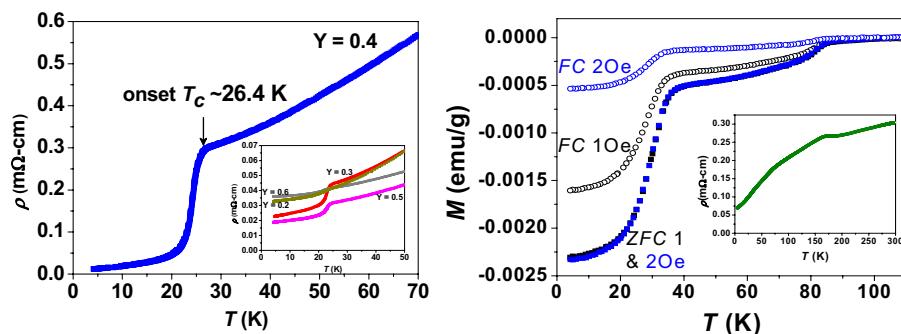


Fig. 1  $R$ - $T$  of  $Sr_{1-x}Y_xFe_2As_2$  (a) and  $M$ - $T$  of  $Ca_{0.7}Y_{0.3}Fe_2As_2$  displaying superconducting-like magnetic transition at 84 and 37 K (b).

**References :**

- [1] Y. Kamihara *et al.*, J. Am. Chem. Soc. Vol. 130 (2008) 3296.
- [2] K. Sasmal *et al.*, Phys. Rev. Lett. 101 (2008) 107007; M. Rotter *et al.*, Vol. 101 (2008) 107006; G.F. Chen *et al.*, Chin. Phys. Lett. Vol. 25 (2008) 3403.

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<b>Home Page:</b> <a href="http://kadowaki.ims.tsukuba.ac.jp/Int/index.htm">http://kadowaki.ims.tsukuba.ac.jp/Int/index.htm</a>	
<b>Presentation Title:</b> Several microwatt level of emission from rectangular shape Bi2212 mesa -improvement in radiation power and towards the realization of THz generator-	
<b>Abstract:</b> <p>Monochromatic and continuous THz radiation from Bi2212 intrinsic Josephson junctions (IJJs) has intensively been studied over the past 2 years [1]. It has been disclosed so far that two conditions are important for THz radiation from IJJ's mesa. One is the <i>ac</i> Josephson effect, and the other is the cavity resonance. It is known that the mW level of power is needed for the practical applications, however, experimentally the available power of radiation is about 5 <math>\mu</math>W [2].</p> <p>Herein, we report here a considerable improvement of the emission power compared with previous reports. Figure 1 shows the <i>I</i>-<i>V</i> characteristics and the emitted radiation from a 1.5 to 2.0 <math>\mu</math>m thick mesa detected by the Si-composite bolometer. The THz emission occurs only in the retrapping region in the return branch from above <math>T_c</math>. When the <i>I</i>-<i>V</i> curve reaches a particular current-voltage state, considerably strong emission was observed. From measurement of the angular dependence of radiation, the total emitted power was roughly estimated to be 50 <math>\mu</math>W. This emission is reproducible but unstable. Although the reason for this strong radiation is not yet understood well, 10 times more powerful emission implies that the THz solid generator is much more promising for practical applications.</p> <p>This work has been performed in close collaboration with the group of Dr. Wai -K. Kwok at the Argonne National Laboratory under JSPS Core-to-Core Program-Strategic Research Networks, "Nanoscience and Engineering in Superconductivity (NES)". We also thank Prof. Y. Ootuka at Univ. of Tsukuba, for his help with the photolithography experiment and the use of the facility.</p>	
<b>References :</b> (1) L. Ozyuzers <i>et al.</i> , Science <b>318</b> (2007) 1291. (2) K. Kadowaki <i>et al.</i> , Physica <b>C 468</b> (2008) 634.	

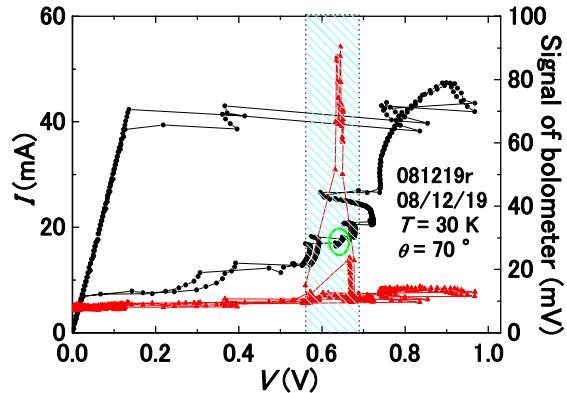


Fig1. *I*-*V* characteristics and emitted radiation detected by Si-composite bolometer. Strong emission was observed at  $V = 0.644$  V. This output power was considerably increased by 10 times stronger than previous reports.

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Preparation of Nitrogen-Doped Lamellar Solid Acids with Visible Light-Responsive Photocatalytic Activities

**Abstract:**

Semiconductor photocatalysis is currently attracting increasing interest in both scientific and engineering areas [1]. In view of the better utilization of the solar light and the indoor illumination, it is appealing to develop visible light-sensitive photocatalysts. Thus, some new photocatalysts with visible light responsibilities have been developed in the recent years [2]. Solid acids are among the most important compounds in materials science, and have a large number of applications like catalysts, ion conductors, and electrode materials. Ti- and Nb-based lamellar solid acids are more attractive because of some particular properties like the layered structure, favorable electron-transfer character, and the protonic acidity. In the present study, two lamellar solid acids, viz.  $\text{HNb}_3\text{O}_8$  and  $\text{H}_2\text{Ti}_4\text{O}_9$ , had been successfully doped with nitrogen by a facile solid state-reaction method with urea as a nitrogen precursor [3]. The nitrogen-doped solid acids show superior activities for Rhodamine B photodegradation than the corresponding nitrogen-doped potassium salts under visible light irradiation (Figure 1). It was revealed that the intercalation properties of lamellar solid acids could have profound impacts on nitrogen doping as well as the resultant visible light photocatalysis, and the effects depend strongly on the protonic acidities of samples.

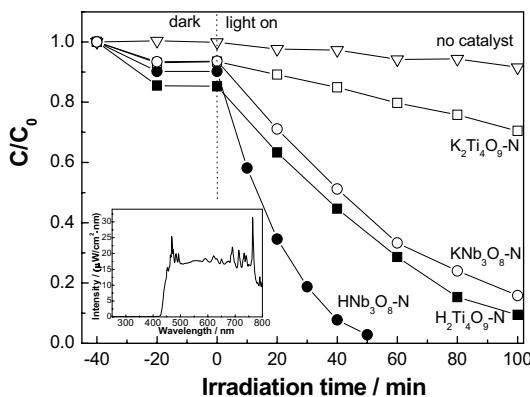
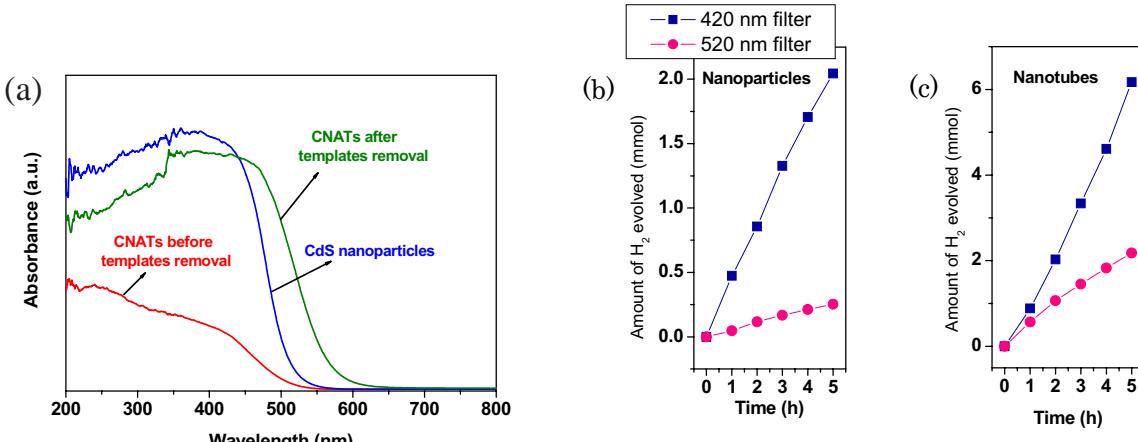
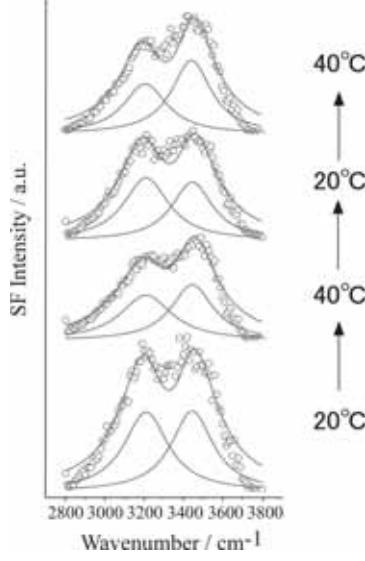


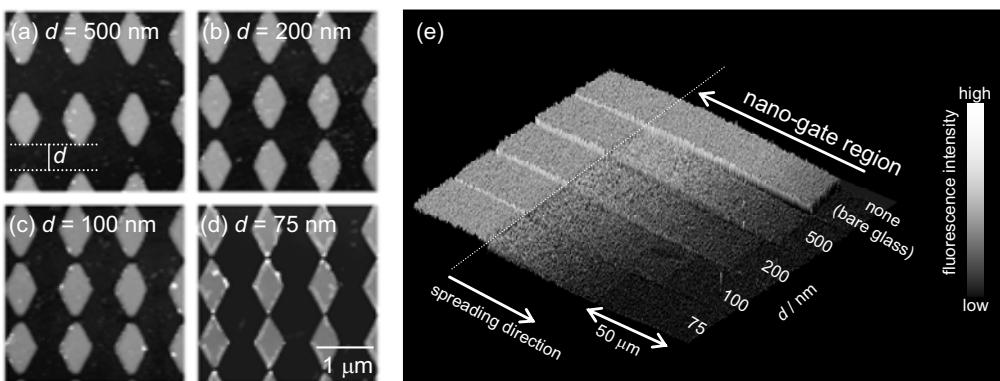
Fig. 1. The photocatalytic degradation of RhB over various nitrogen-doped niobates and titanates under visible light ( $\lambda > 420$  nm) irradiation.

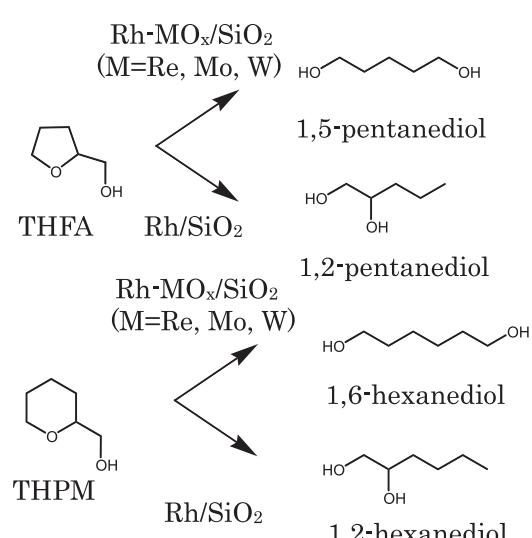
**References:**

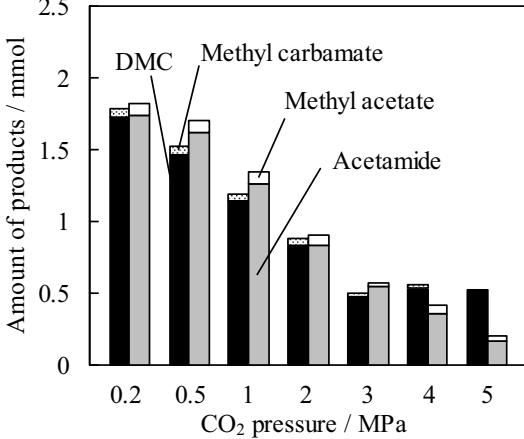
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2. X. Li, J. Ye, J. Phys. Chem. C 111 (2007) 13109.
3. X. Li, N. Kikugawa, J. Ye, Adv. Mater., 20 (2008) 3816.

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<b>Presentation Title:</b> Semiconductor Nanoparticle Assemblies: Adjustable Band Gap and Photocatalytic Applications	
<b>Abstract:</b> <p>The materials with size in nanoscale could have adjustable bandgap, high efficiency in absorbing photons and larger surface ratio, which are very valuable for improving their photocatalytic performance. As a typical direct gap semiconductor, cadmium sulfide has suitable band gap and relatively negative conduct band potential to be used as catalyst for producing hydrogen under irradiation of visible light.<sup>1, 2</sup> In this work, we found that not only the CdS nanoparticles have high photocatalytic activity, but also the CdS nanoparticles assembled tubes (CNATs) have even higher photocatalytic activity due to red-shift of absorption edge.</p>	
 <p><b>(a)</b> UV-visible diffuse reflectance spectra showing Absorbance (a.u.) vs. Wavelength (nm) for CdS nanoparticles (blue line) and CNATs before (red line) and after (green line) template removal. The CNATs show a significant redshift in absorption edge compared to CdS nanoparticles.</p> <p><b>(b)</b> Time course of hydrogen evolution (mmol) for 0.1 g CdS nanoparticles under light irradiation from a 300 W Xe-lamp equipped with cutoff filter L42 and a water filter. The amount of H<sub>2</sub> evolved increases over time, with a higher rate initially and then leveling off.</p> <p><b>(c)</b> Time course of hydrogen evolution (mmol) for 0.1 g CNATs under the same conditions. The CNATs show a significantly higher rate of hydrogen evolution compared to CdS nanoparticles, reaching a higher total amount of H<sub>2</sub> evolved by 5 hours.</p>	
<p>Fig. 1 (a) UV-visible diffuse reflectance spectra of CdS nanoparticles and CNATs, time course of hydrogen evolution of 0.1 g CdS nanoparticles (b) and CNATs (c), respectively, under light irradiation from a 300 W Xe-lamp equipped with cutoff filter L42, L52 and a water filter.</p>	
<b>References:</b> <ul style="list-style-type: none"> <li>(1) N. Bao, L. Shen, T. Takata, K. Domen, <i>J. Phys. Chem. C</i>, 2007, <b>111</b>, 17527-34.</li> <li>(2) N. Bao, L. Shen, T. Takata, K. Domen, <i>Chem. Mater.</i>, 2008, <b>20</b>, 110–117.</li> </ul>	

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<b>Presentation Title:</b> Interfacial molecular structure at solid/liquid interfaces by surface sensitive vibrational spectroscopies.	
<b>Abstract:</b> Molecular level characterization of the structure of proteins and many other biomaterials, especially in wet conditions, are quite important to understand how they function. We applied surface specific vibrational spectroscopies (SFG and ATR-IR) to investigate the structure and function of (1) interfacial water at thermo-responsive polymer surface and (2) protein immobilized on solid surface in buffer solution.	
<b>1. Interfacial water structure at PNIPAM surface studied by SFG spectroscopy</b> Poly-N-isopropyl-acrylamide (PNIPAM) is one of the most thoroughly investigated thermo-responsive polymers in aqueous solution. PNIPAM has a well defined lower critical solution temperature (LCST) around 32°C. Below LCST, PNIPAM chains are strongly hydrated with water molecules. Above the LCST, they dehydrate and collapse to a globular form. Such structural transition induced by temperature may have a number of interesting possible applications. However, the detail molecular information especially about the water molecules around PNIPAM chains is still controversial. In this study, temperature dependence of interfacial water structure at PNIPAM surface was investigated by SFG spectroscopy. SFG spectra in the OH stretching region of PNIPAM/water interface are shown in Figure 1. Two broad peaks were observed at ca. 3200 $\text{cm}^{-1}$ and ca. 3450 $\text{cm}^{-1}$ , which are known to be due to the symmetric OH stretching of strongly hydrogen bonded water "ice-like water" and the asymmetric OH stretching of weakly hydrogen bonded water "liquid-like water", respectively. SFG intensity of the "liquid-like water" component became stronger as the temperature increased from 20 to 40°C. When the temperature was decreased to 20°C, SFG spectrum returned to the initial shape. These results suggest that the PNIPAM surface reversibly changes from "hydrophobic" to "hydrophilic" as the temperature changes from 20 to 40°C.	<p>Fig. 1 SFG spectra of OH stretch region of PNIPAM/water interface at several temperatures.</p> <p>Calmodulin (CaM), which is one of the <math>\text{Ca}^{2+}</math> binding protein, immobilized on a chemically modified gold surface by binding its histidine-tag to surface attached nickel-chelating nitrilo-triacetic acid (Ni-NTA), maintaining its activities. Association and dissociation of target peptide mastoparan(MP) with the immobilized CaM was monitored in real time using in situ ATR-IR spectroscopy by varying the concentration of MP to estimate the binding constant of MP with immobilized CaM. The binding constant was 4 orders of magnitude smaller than homogeneous system, suggesting that the conformational change of CaM was sterically hindered by surface immobilization. Effect of <math>\text{Ca}^{2+}</math> on the structure of water around CaM was also investigated by using SFG.</p>
<b>2. Structure and function of calmodulin immobilized on a solid substrate studied by in situ ATR-IR and SFG spectroscopies</b> Calmodulin (CaM), which is one of the $\text{Ca}^{2+}$ binding protein, immobilized on a chemically modified gold surface by binding its histidine-tag to surface attached nickel-chelating nitrilo-triacetic acid (Ni-NTA), maintaining its activities. Association and dissociation of target peptide mastoparan(MP) with the immobilized CaM was monitored in real time using in situ ATR-IR spectroscopy by varying the concentration of MP to estimate the binding constant of MP with immobilized CaM. The binding constant was 4 orders of magnitude smaller than homogeneous system, suggesting that the conformational change of CaM was sterically hindered by surface immobilization. Effect of $\text{Ca}^{2+}$ on the structure of water around CaM was also investigated by using SFG.	

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<b>Presentation Title:</b> Single Molecule Manipulation in a Lipid Bilayer using Metal Nanogates	
<p><b>Abstract:</b></p> <p>Molecular manipulation at the nanometer dimension is one of the technological goals for ultra-sensitive molecular manipulation systems at ultra-small devices. Especially for bio-materials, manipulation on a lipid bilayer is a wildly acceptable candidate as a medium due to its ability to manipulate the bio-materials in their native environment. Recent activity has focused on an electrophoretic manipulation of lipids, vesicles, and proteins. Despite these growing developments, the electrophoresis imposes restriction in that only charged molecules can be manipulated. To overcome this limitation, a self-spreading lipid bilayer can be used as an alternative tool for the molecular transportation [1]. The lipid bilayer self-spreading is a thermodynamically driven collective molecular flow on a solid surface, in which there is no need to input any bias to induce the molecular flow. The self-spreading bilayer can transport any molecule on the bilayer, even non-charged molecules, in any direction.</p> <p>We have reported the molecular filtering phenomena of the self-spreading lipid bilayer using a nanogate substrate [2], in which the bilayer continuously spread through the nanogate (Fig. 1). During spreading on the nanogate channel, the fluorescence intensity, i.e., the concentration of the doped dye-labeled lipid in the bilayer, was apparently attenuated. This filtering phenomenon became more evident with decreasing the gate width <math>d</math>. Taking into account the two-dimensional elastic nature of the lipid bilayer, the filtering phenomena would be brought from the formation of a compressed bilayer state at the gate during spreading through. The formation of the compressed phase imposes a local chemical potential barrier at the gate, which is supposed to be a principal basis that lead the reduction in the penetration ability of the doped molecules at the gate.</p>	
	
<p>Fig. 1. (a)-(d) AFM images of nanogate with difference gate-width <math>d</math>. (e) 3-D images of fluorescence micrograph for the self-spreading lipid bilayer doped with dye-labeled lipid on each nano-gate channel.</p>	
<p><b>References:</b></p> <p>[1] H. Nabika, A. Fukasawa, K. Murakoshi, <i>Langmuir</i>, <b>22</b>, 10927-10931 (2006).      [2] (a) H. Nabika, A. Sasaki, B. Takimoto, Y. Sawai, S. He, K. Murakoshi, <i>J. Am. Chem. Soc.</i>, <b>127</b>, 16786 (2005). (b) H. Nabika, N. Iijima, B. Takimoto, K. Ueno, H. Misawa, K. Murakoshi, <i>Anal. Chem.</i> in press (2009).</p>	

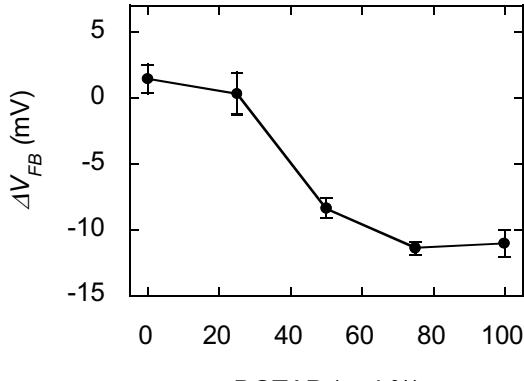
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<b>Presentation Title:</b> Chemoselective hydrogenolysis of tetrahydrofurfuryl alcohol to 1,5-pentanediol	
<p><b>Abstract:</b>            Utilization of biomass as a renewable raw material will gain importance in the industrial production of chemical substances for sustainability and as a substitute for petroleum for energy production. Since biomass-related raw materials usually have high oxygen content, useful oxygenates such as terminal-diols will be one of target chemicals derived from biomasses. Terminal-diols, which have a linear carbon-carbon chain and carbons at both edges with the OH group, are mainly made from petroleum and they have been used as monomers for the production of polyesters and polyurethanes. Tetrahydrofurfuryl alcohol (THFA) and tetrahydropyran-2-methanol (THPM) were derived from hemi-cellulose and glycerol, respectively. The objective of the research is to develop effective catalysts for the production of 1,5-pentanediol and 1,6-hexanediol from THFA or THPM.         </p> <p>We found that Rh-MO<sub>x</sub>/SiO<sub>2</sub> (M=Re, Mo, W) catalysts are much more active and selective in the hydrogenolysis of THFA and THPM to 1,5-pentanediol and 1,6-hexanediol than conventional hydrogenolysis catalysts, respectively. These reaction schemes show Scheme 1. In the hydrogenolysis of THFA, Rh-ReO<sub>x</sub>/SiO<sub>2</sub> gave 86% yield of 1,5-pentanediol. The activity of Rh/SiO<sub>2</sub> is rather low and a main product is 1,2-pentanediol. The modification of Rh/SiO<sub>2</sub> with ReO<sub>x</sub> switched the main product from 1,2-pentanediol to 1,5-pentanediol. At the same time, it enhanced the catalytic activity in the hydrogenolysis drastically. The Rh-ReO<sub>x</sub>/SiO<sub>2</sub> also gave 77% yield of 1,6-hexanediol in the hydrogenolysis of THPM and the tendency of the additive effect of ReO<sub>x</sub>, MoO<sub>x</sub> and WO<sub>x</sub> on the product selectivity was similar to the case of THFA. Results of various characterizations, we think that the interaction of -CH<sub>2</sub>OH groups in the reactants with MO<sub>x</sub> located on Rh metal particles promotes chemoselective hydrogenolysis over Rh metal surface to terminal-diols.         </p>	
 <p style="text-align: center;">Scheme Main reaction route in the hydrogenolysis of THFA or THPM</p>	

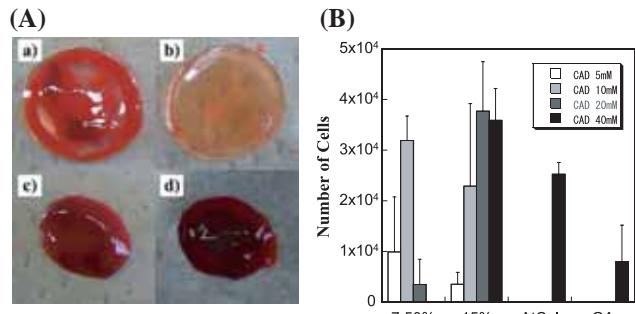
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<b>Presentation Title:</b> Development of catalytic process of CO <sub>2</sub> conversion to organic carbonate																																									
<b>Abstract:</b> Dimethyl carbonate (DMC) has attracted much attention as an environmentally benign substitute for phosgene and widely used as a starting material of polycarbonate resin. It has been reported that selective synthesis of DMC from CH <sub>3</sub> OH and CO <sub>2</sub> catalyzed by CeO <sub>2</sub> <sup>1-3)</sup> . However, the methanol and CO <sub>2</sub> conversion is limited to be rather low because of the reaction equilibrium. We report that acetonitrile (AN) hydration reaction enhanced the DMC yield drastically, in particular, under low CO <sub>2</sub> pressure when AN is introduced to the reaction system.																																									
<div style="display: flex; align-items: center; justify-content: space-between;"> <div style="flex: 1;"> <math display="block">2 \text{CH}_3\text{OH} + \text{CO}_2 \xrightleftharpoons[\text{CeO}_2]{\text{CeO}_2} \text{H}_3\text{C}-\text{O}-\text{C}(=\text{O})-\text{O}-\text{CH}_3 \quad \text{DMC}</math> <math display="block">\text{H}_3\text{C}-\text{O}-\text{C}(=\text{O})-\text{O}-\text{CH}_3 + \text{CH}_3\text{CN} \xrightleftharpoons[\text{CeO}_2]{\text{CeO}_2} \text{H}_3\text{C}-\text{C}(=\text{O})-\text{NH}_2 \quad \text{Acetamide}</math> <math display="block">\text{H}_3\text{C}-\text{C}(=\text{O})-\text{NH}_2 + \text{CH}_3\text{OH} \xrightleftharpoons[-\text{NH}_3]{\text{CeO}_2} \text{H}_3\text{C}-\text{O}-\text{CH}_3 \quad \text{Methyl acetate}</math> </div> <div style="flex: 1; text-align: center;"> <p>Reaction scheme</p> </div> </div>	 <table border="1"> <caption>Data for Figure 1: Effect of CO<sub>2</sub> pressure on product amounts</caption> <thead> <tr> <th>CO<sub>2</sub> pressure / MPa</th> <th>DMC / mmol</th> <th>Methyl carbamate / mmol</th> <th>Methyl acetate / mmol</th> <th>Acetamide / mmol</th> </tr> </thead> <tbody> <tr> <td>0.2</td> <td>~1.8</td> <td>~1.8</td> <td>~1.8</td> <td>~1.8</td> </tr> <tr> <td>0.5</td> <td>~1.5</td> <td>~1.7</td> <td>~1.7</td> <td>~1.7</td> </tr> <tr> <td>1</td> <td>~1.2</td> <td>~1.3</td> <td>~1.3</td> <td>~1.2</td> </tr> <tr> <td>2</td> <td>~0.9</td> <td>~0.9</td> <td>~0.9</td> <td>~0.9</td> </tr> <tr> <td>3</td> <td>~0.5</td> <td>~0.6</td> <td>~0.6</td> <td>~0.5</td> </tr> <tr> <td>4</td> <td>~0.5</td> <td>~0.4</td> <td>~0.4</td> <td>~0.5</td> </tr> <tr> <td>5</td> <td>~0.2</td> <td>~0.2</td> <td>~0.2</td> <td>~0.2</td> </tr> </tbody> </table>	CO <sub>2</sub> pressure / MPa	DMC / mmol	Methyl carbamate / mmol	Methyl acetate / mmol	Acetamide / mmol	0.2	~1.8	~1.8	~1.8	~1.8	0.5	~1.5	~1.7	~1.7	~1.7	1	~1.2	~1.3	~1.3	~1.2	2	~0.9	~0.9	~0.9	~0.9	3	~0.5	~0.6	~0.6	~0.5	4	~0.5	~0.4	~0.4	~0.5	5	~0.2	~0.2	~0.2	~0.2
CO <sub>2</sub> pressure / MPa	DMC / mmol	Methyl carbamate / mmol	Methyl acetate / mmol	Acetamide / mmol																																					
0.2	~1.8	~1.8	~1.8	~1.8																																					
0.5	~1.5	~1.7	~1.7	~1.7																																					
1	~1.2	~1.3	~1.3	~1.2																																					
2	~0.9	~0.9	~0.9	~0.9																																					
3	~0.5	~0.6	~0.6	~0.5																																					
4	~0.5	~0.4	~0.4	~0.5																																					
5	~0.2	~0.2	~0.2	~0.2																																					

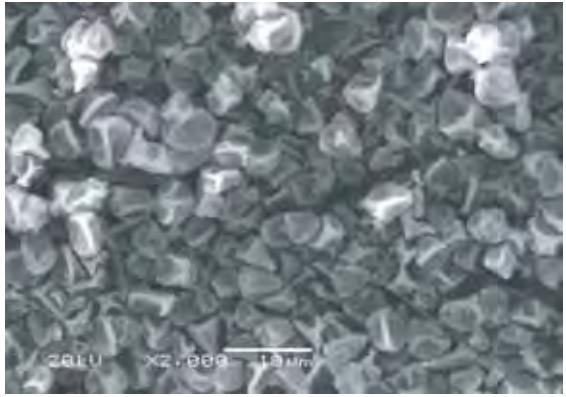
The amount of DMC formation gradually increased with decreasing CO<sub>2</sub> pressure. According to previous reports, however, the direct synthesis of DMC from methanol and CO<sub>2</sub> has been usually carried out under very high CO<sub>2</sub> pressure such as 5 MPa. The DMC formation at low CO<sub>2</sub> pressure is associated with the AN hydration to acetamide which is also catalyzed by CeO<sub>2</sub>. High pressure of CO<sub>2</sub> inhibits the AN hydration on CeO<sub>2</sub>, in contrast, the reaction route is open under low CO<sub>2</sub> pressure.

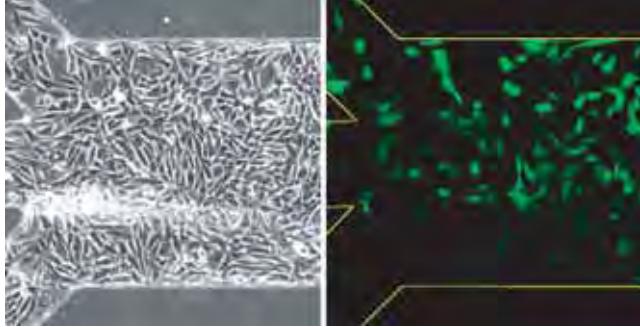
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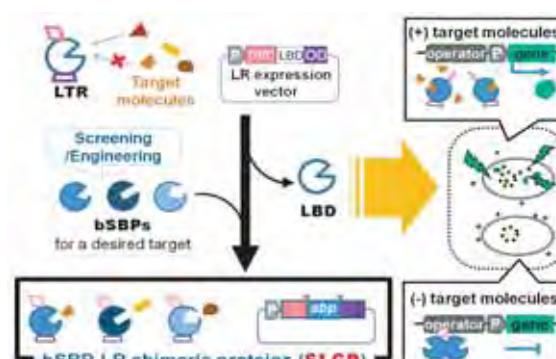
- 1) K.Tomishige, Y.Furusawa, Y.Ikada, M.Asadullah and K.Fujimoto, *Catal. Lett.*, **76**, 71 (2001).
- 2) K. Tomishige and K. Kunimori, *Appl. Catal. A*, **237**, 103 (2002).
- 3) Y. Yoshida, Y. Arai, S. Kado, K. Kunimori and K. Tomishige, *Catal. Today*, **115**, 95 (2006).

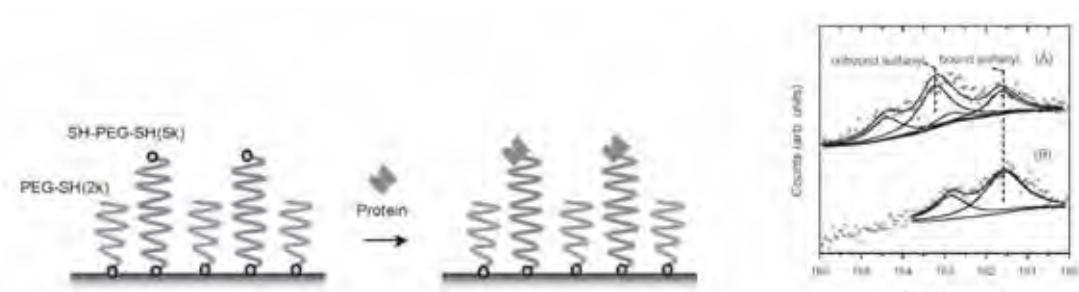
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<b>Home Page:</b>													
<b>Presentation Title:</b> Detection of Supported Lipid Bilayers Using Their Electric Charge													
<b>Abstract:</b> <p>The electric charge of lipids plays crucial roles in biochemical processes. Charged lipids can sometimes be incorporated into supported lipid bilayers (SLBs) by vesicle fusion. Since SLBs are useful in vitro mimics for biological membranes, their properties and formation mechanisms have been widely studied by monitoring various signals including fluorescence, mass, viscoelasticity, refractive index, topography, and impedance. In this study, SLBs were detected through their charge using field-effect devices. The field-effect sensing technique has been employed for various analytes including polymers and DNA. Similarly, field-effect devices might potentially serve as biosensors for analyzing molecular recognition events involving lipid membranes. However, little is known about the field effect of SLB systems.</p>	 <table border="1"> <caption>Data points estimated from Figure 1</caption> <thead> <tr> <th>DOTAP (mol %)</th> <th><math>\Delta V_{FB}</math> (mV)</th> </tr> </thead> <tbody> <tr><td>0</td><td>1</td></tr> <tr><td>25</td><td>0</td></tr> <tr><td>50</td><td>-7</td></tr> <tr><td>75</td><td>-11</td></tr> <tr><td>100</td><td>-11</td></tr> </tbody> </table>	DOTAP (mol %)	$\Delta V_{FB}$ (mV)	0	1	25	0	50	-7	75	-11	100	-11
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100	-11												
<b>Fig. 1.</b> Planar DOTAP/DOPC bilayers. Buffer: 20 mM KCl, 10 mM potassium phosphate, pH 8.0.													
<b>Reference:</b>													
[1] C. Kataoka-Hamai, H. Inoue, and Y. Miyahara, Langmuir 24 (2008) 9916.													

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<b>Presentation Title:</b> Improved anti-thrombogenic and endothelial cell adhesive properties of citric acid-crosslinked collagen																											
<b>Abstract:</b> Drug-eluting stents (DES) prevent in-stent restenosis by eluting drugs from matrices on DES to suppress smooth muscle cell growth. However, the residual matrices on DES lead to complications such as exaggerated inflammatory response, thrombus formation, and prevention of endothelialization at the implant site after the drug elutes from the matrices. Therefore, it is necessary to develop a novel biodegradable matrix with both anti-thrombogenic and endothelial cell adhesion after the drug elution. We previously developed a novel crosslinker citric acid derivative (CAD) with three active ester groups in order to prepare biopolymer-based materials [1-3]. In the present study, we report on a novel biodegradable matrix which has anti-thrombogenic and cell adhesion properties; the study was part of our ongoing research on the matrices for drug-eluting stents. Using alkali-treated collagen (AlCol) and CAD (AlCol-CAD), we evaluated the physicochemical properties such as swelling ratio, residual amino groups, and carboxyl groups of the resulting AlCol-CAD in order to clarify influence of thrombus formation and cell adhesion [4]. In vitro and in vivo evaluation of drug-encapsulated AlCol-CAD was also performed. Fig. 1(A) shows the effect of CAD concentration on thrombus formation of 15 w/v% AlCol-CAD. Significant thrombus formation was observed on AtCol gel, AlCol-GA, and AlCol-CAD (5 mM) after immersion in rat arterial blood. Fig. 1(B) shows the adhesion number of HUVECs on 7.5, and 15 w/v% AlCol-CAD with different CAD concentrations. Aterocollagen (AtCol) gel and AlCol-glutaraldehyde (GA) were used as control materials. The adhesion number of HUVECs on 15 w/v% AlCol-CAD increased with increase in CAD concentration up to 20 mM, and then decrease with further increase in CAD concentration. These results suggested that the 15w/v% AlCol-CADs with higher CAD concentration than 20mM have great potential as matrices for DES.	<p>Fig. 1 (A) Photographs of AlCol-CADs at different CAD concentrations after immersion of gels in rat arterial blood (a) 5 mM; (b) 20 mM; (c) AtCol gel; (d) AlCol-GA. (B) Number of HUVECs adhered on AtCol gel, AlCol-GA and AlCol-CAD at different CAD concentrations.</p>  <table border="1"> <caption>Data for Figure 1(B): Number of HUVECs adhered on AtCol gel, AlCol-GA and AlCol-CAD at different CAD concentrations</caption> <thead> <tr> <th>Material</th> <th>CAD Concentration (mM)</th> <th>Number of HUVECs (approx.)</th> </tr> </thead> <tbody> <tr> <td rowspan="4">AtCol</td> <td>5</td> <td>1.0 x 10<sup>4</sup></td> </tr> <tr> <td>10</td> <td>3.0 x 10<sup>4</sup></td> </tr> <tr> <td>20</td> <td>3.5 x 10<sup>4</sup></td> </tr> <tr> <td>40</td> <td>2.5 x 10<sup>4</sup></td> </tr> <tr> <td rowspan="2">AlCol-GA</td> <td>5</td> <td>1.0 x 10<sup>4</sup></td> </tr> <tr> <td>10</td> <td>3.0 x 10<sup>4</sup></td> </tr> <tr> <td rowspan="4">AlCol-CAD</td> <td>5</td> <td>1.0 x 10<sup>4</sup></td> </tr> <tr> <td>10</td> <td>3.0 x 10<sup>4</sup></td> </tr> <tr> <td>20</td> <td>3.5 x 10<sup>4</sup></td> </tr> <tr> <td>40</td> <td>2.5 x 10<sup>4</sup></td> </tr> </tbody> </table>	Material	CAD Concentration (mM)	Number of HUVECs (approx.)	AtCol	5	1.0 x 10 <sup>4</sup>	10	3.0 x 10 <sup>4</sup>	20	3.5 x 10 <sup>4</sup>	40	2.5 x 10 <sup>4</sup>	AlCol-GA	5	1.0 x 10 <sup>4</sup>	10	3.0 x 10 <sup>4</sup>	AlCol-CAD	5	1.0 x 10 <sup>4</sup>	10	3.0 x 10 <sup>4</sup>	20	3.5 x 10 <sup>4</sup>	40	2.5 x 10 <sup>4</sup>
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<b>Acknowledgement:</b> This work was financially supported in part by grant-in-aid from National Institute of Biomedical Innovation, Japan.																											
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1) T. Taguchi, et al., <i>J. Nanosci. Nanotechnol.</i> , 7, 742, 2007., 2) T. Taguchi, et al., <i>Mater. Sci. Eng. C</i> , 24, 775, 2004. 3) H. Saito and T. Taguchi, et al., <i>Acta Biomater.</i> , 3, 89, 2007., 4) H. Saito and T. Taguchi, et al., <i>Biomacromolecules</i> , 8, 1992, 2007.																											

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<b>Presentation Title:</b> Electrospray Deposition as a New Method for Preparing Fine Drug Particles	
<b>Abstract:</b> Although there has been much discussion on favorable physicochemical properties for drug candidates over the last decade, formulators must still deal with many challenging compounds including poorly soluble drugs. A novel formulation technology, electrospray deposition method, is introduced in this presentation. This method enabled amorphization and micronization of the formulation, both of which contribute to improvement of the solubility, in one-step preparation procedure.	
<p>Electrospray Deposition (called as “Electrospinning” in polymer science field) has been regarded as a promising method to prepare various fibrous materials such as filters, sensors, and many types of biomedical materials. Various poorly soluble drugs including prednisolone (PDN), phenylbutazone, phenytoin and carbamazepine were dissolved with polymeric carriers including polyvinylpyrrolidone (PVP), Eudragid E-100, and polyethylene glycol either in ethanol or in its aqueous solution. The solutions were introduced to 8-pin manifold using a syringe pump, followed by application of high voltage, typically in the range of 10-25 kV, to produce electrospray to a stainless steel target. The setup was enclosed in an air-tight box to control humidity of the environment. The dried particles were collected from the target surface.</p> <p>Figure shows an example of the SEM picture of the particles prepared by this method. Typically, the particle had very unique shape with its size of around a few micrometer. The unique shape might be elucidated in terms of rapid formation of the polymer film on the droplet surface, followed by removal of the solvent and the shrinkage of the droplet. The particle was in the amorphous state in most cases except that crystal structure was obtained when carbamazepine was used as a model drug. In that case, the unique shape was lost to form almost spherical shape, probably because of the molecular rearrangement after the deposition. The greatest advantage of this method as a formulation technology is that it can be operated at ambient temperature, because other methods for preparing amorphous formulations require very severe conditions such as high temperature that may cause degradation of the drug.</p>	
 <p>Figure: Particles of PVP/PDN=1/1(w/w)</p>	

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<b>Presentation Title:</b> Live cell-based sensor devices	
<b>Abstract:</b> <p>Living cells maintain life functions by responding quickly and with great sensitivity to changes in the external environment. Consequently, sensors using cells as active elements are thought to be able to perform analyses faster and with more sensitivity than previously possible.</p> <p>We report here a live cells-based sensorchip fabricated in microfluidic channels in which several laminar flows were achieved. In addition, we established a cytotoxic sensor cell line, which was transfected with a green fluorescence protein (GFP) plasmid derived from the heat shock protein 70B' (HSP70B') promoter, which is induced by cytotoxic reagents [1-4]. The fluorescence in the sensor cells increased in a CdCl<sub>2</sub> dose-dependent manner in the microfluidic channels [5,6]. In this system, cytotoxic reagents can be quantitatively detected in a quick, sensitive and high- throughput manner. The combination of sensor cells and microfluidic systems will provide an important basis for the development of micro-total analysis systems (micro-TAS) technology, and can be applied to toxicology, environmental assessment and drug screening.</p>	
	
Fig.1 Cells-based sensorchip fabricated in microfluidic channels.	
<b>References:</b>	
[1] Okuda-Shimazaki J, Taniguchi A. et al., Open Biotechnol J 2007; 1:1-4.	
[2] Wada KI, Taniguchi A, Xu LM, Okano T. Biotechnol Bioeng 2005; 92: 410-5.	
[3] Wada KI, Taniguchi A, Okano T. Biotechnol Bioeng 2007; 97,871-876.	
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[6] Wada KI, Taniguchi A, Okano T. Biotechnol Bioeng 2008; 99, 1513-1517.	

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<b>Presentation Title:</b> Building a novel transcriptional regulator as a universal switch platform	
<p><b>Abstract:</b>            Transcriptional regulators activated by the target molecule interact with the promoter triggering production of the functional proteins. Utilizing transcriptional regulators, biosensors, transgenic expression systems, and signal amplification cascades can be constructed that detect compounds as varied as those related to quorum sensing. Engineering of target molecule-binding site of transcriptional regulator to enhance sensitivity and specificity to target molecules have been reported. We have also proposed a novel design and construction method for engineered transcriptional regulators.</p> <p>Bacterial substrate binding proteins (bSBPs) have been focused as novel probes to biosensing and biosensors. bSBPs have been identified for a wide variety of ligands with high affinity (<math>K_d</math> = approx. <math>10^{-6}</math> M). Most bSBPs have a similar structural consisting of two domains linked by a hinge region and undergo a large conformational change by ligand binding. The developments of bSBP-based sensing systems are recently reported by screening of novel bSBPs for desired target or by genetic engineering to improve its binding properties, etc. bSBPs have thus great possibility to be a universal probe which can be applied to sensing systems for variety of ligands.</p> <p>Here we report our novel approach in the design and construction of engineered transcriptional regulators based on engineered bSBPs as target molecule recognition elements. We designed bSBP-based regulators, bSBP-LTR chimeric proteins (SLCP) combined one of bSBPs with a bSBP-like regulator, LacI-like repressor proteins (LTR), which consists of DNA-binding domain and substrate binding domain similar to bSBPs A chimeric protein of well analyzed bSBP, galactose-/glucose -binding protein (GBP), and LacI from <i>Escherichia coli</i> was at first selected as a model of bSBP-based regulators and constructed based on 3-D structural models. We also show the characterization of the constructed GBP-LacI chimeric protein as a transcriptional regulator in vitro and in mammalian cells.</p>	
 <p>Figure Construction of novel transcriptional regulators</p>	

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<b>Presentation Title:</b> Bioreactivity of PEGylated gold surfaces constructed by mixed homo-/hetero-telechelic PEGs	
<b>Abstract:</b> Improved method for functionalizing surfaces with bioactive molecules, retaining the excellent non-fouling character, would accelerate the development of immunoassays, diagnostics, and tissue engineering applications. We present herein new strategies for constructing bioactive molecules-terminated surfaces with excellent nonfouling character by homo-/hetero-telechelic poly(ethylene glycol)s (PEGs). Sulfanyl-terminated PEGylated gold surfaces was constructed by the combined use of a longer-homo-telechelic PEG, $\alpha,\omega$ -disulfanyl PEG (SH-PEG-SH(5k)), and shorter-semi-telechelic PEG, $\alpha$ -methoxy- $\omega$ -sulfanyl PEG (MeO-PEG-SH(2k)) [1]. This consecutive treatment prevents a loop formation of SH-PEG-SH(5k) on the gold surface. On the constructed MeO-PEG-SH (2k)/SH-PEG-SH (5k) mixed tethered-chain surface, the selective immobilization of Fab' fragment and maleimide group-containing protein were demonstrated as shown in Figure 1 and evaluated by surface plasmon resonance (SPR) spectroscopy. The protein-installed SH-PEG-SH (5k)/MeO-PEG-SH (2k)-modified surface recognized the target molecules selectively and showed a fairly low non-specific protein adsorption as strong as that of the conventional MeO-PEG-SH (5k)/MeO-PEG-SH (2k) mixed surface, which showed a superior non-fouling characteristic in our previous work [2]. We also established a technique for constructing PEGylated gold nanoparticle (GNP), which possessed small compounds on their surfaces with high level functionalities, using hetero-telechelic PEG, $\alpha$ -sulfanyl- $\omega$ -amino-PEG (SH-PEG-NH <sub>2</sub> ). SPR analysis revealed that the PEGylated GNP with 4 % of antigen functionalities showed small binding affinity on antibody Fab' immobilized sensor surface and dissociation behavior from the surface was observed by the competitive reaction of free antigen. In contrast, the constructed PEGylated GNPs with 30-100 % of antigen functionalities on its surface had a high binding affinity accompanying with nondissociative property on antibody Fab' immobilized sensor surface [3]. These results indicated that the surface functionalization techniques using homo/hetero-telechelic PEGs provided a bioreactive surfaces with excellent binding properties and nonfouling character.	
	
Fig.1 Schematic illustration of protein immobilization on SH-terminated Mixed-PEG(2k/5k) modified gold surface (left). Xray-photospectroscopy S2p spectra (right, A) of SH-terminated Mixed-PEG(2k/5k) surface and the conventional MeO-PEG-SH (2k)/MeO-PEG-SH (5k) mixed tethered-chain gold surface (right, B).	
<b>References:</b>	
[1] <u>Yoshimoto K.</u> , Hirase T., Nemoto S., Hatta T., Nagasaki Y., <i>Langmuir</i> , 24 (2008) 9623.	
[2] Uchida K., Hoshino Y., Tamura A., <u>Yoshimoto K.</u> , Kojima S., Yamashita K., Yamanaka I., Otsuka H., Kataoka K., Nagasaki Y., <i>Biointerphases</i> , 2 (2007) 126.	
[3] <u>Yoshimoto K.</u> , Hoshino Y., Ishii T., Nagasaki Y., <i>Chemical Communications</i> , (2008) 5369.	

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<b>Presentation Title:</b> Evaluation of nanomaterials based on molecular biology	
<p><b>Abstract:</b></p> <p>The safety and risk evaluation of nanomaterials has gotten a lot attention recently. Nanomaterials are expected to have the novel physicochemical properties because of their size, chemical composition, surface structure, shape, or aggregation. The novel properties of nanomaterials raise concerns about adverse effects on biological systems. Some recent studies suggest that nanomaterials have potential toxicity and that they affect biological behaviors<sup>1-3</sup>.</p> <p>In this study, nanomaterials, fullerene nanomaterials and titania were investigated about their biocompatibility by molecular biological technique. In order to evaluate the cell response to nanomaterials, we analyze gene expression of biomarkers focused on stress and toxicity.</p> <p>Fullerene nanowhiskers (FNWs) were prepared using the liquid - liquid interfacial precipitation method<sup>4</sup> that layers poor solvent of fullerene (isopropanol) on a fullerene solution prepared by pyridine or toluene.</p> <p>Human acute monocytic leukemia cell line, THP-1 cells were treated with phorbol 12-myristate 13-acetate (PMA)<sup>5</sup>. PMA treated THP-1 or after 24 h from seeding NCI-H292, human mucoepidermoid carcinoma cell line, were exposed by nanomaterials solvent. Total RNA from nanomaterials exposed cells were isolated and reversibly transcribed with random hexamer primer. Real time PCR was performed using specific primer for biomarkers or GAPDH as internal control.</p> <p>RNA expression analysis showed some biomarkers related to inflammation were induced by nanomaterials (Fig.). FNT slightly induced stress markers, however its inducing level was lower than other nanomaterials.</p>	
<p><b>References:</b></p> <ul style="list-style-type: none"> <li>[1] R. F. Service. Science 304 (2004) 1732.</li> <li>[2] G. Oberdörster, E. Oberdörster, J. Oberdörster. Environ. Health Perspect. 113 (2005) 823.</li> <li>[3] C. A. Poland, R. Duffin, I. Kinloch, A. Maynard, W.A. H. Wallace, A. Seaton, V. Stone, S. Brown, W. Macnee, K. Donaldson. Nature Nanotechnology, (AOP) (2008).</li> <li>[4] K. Miyazawa, Y. Kuwasaki, A. Obayashi, J. Mater. Res. 17 (2002) 83.</li> <li>[5] J. Okuda-Shimazaki, A. Yamamoto, D. Kuroda, T. Hanawa, A. Taniguchi, Open Biotechnol. J. 1 (2007) 14.</li> </ul>	

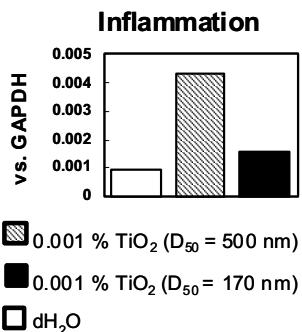
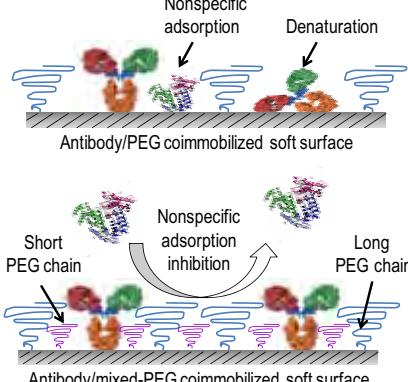


Fig. gene expression of titania exposed cells

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<b>Presentation Title:</b> Construction of a antiferritin/mixed-PEG coimmobilized soft surface onto polystyrene nanospheres to improve its immunodiagnosis performance	
<b>Abstract:</b> Hydrophilic, flexible and neutral poly(ethylene glycol) (PEG) has been widely used to stabilize various nano- and micro-scale particles. In addition, since a PEG chain possesses low affinity for various biomacromolecules, a PEGylated surface improves the performance of biodiagnosis, especially in immunodiagnostic systems. In this case, the long chain length and high chain density of the PEG layer were both required, but increased polymer chain length is always accompanied by decreased polymer chain density, owing to the steric exclusion of the tethered PEG chains. <sup>1</sup> According to our previous investigations of PEGylated surfaces, a mixed-PEG chain layer with both long-chain PEGs and short-chain ones resolved this trade-off relation, in that the long PEG chains retained the chain length of the layer, while the short ones easily occupied the inter-space between two long chains to remarkably increase the total chain density of the layer. <sup>2</sup> ( <b>Scheme 1</b> ) Besides this efficient suppression of various nonspecific interactions, a PEG layer may also create a suitable environment for specific types of bio-recognition. <sup>3</sup> Consequently, a biomacromolecule/PEG, especially a biomacromolecule/mixed-PEG coimmobilized soft surface is considered to be an ideal surface-modification technique for various biosensors, biodiagnosis systems, and so on.	 <p><b>Scheme 1.</b> Antibody/PEG (top) and antibody/mixed-PEG (bottom) soft surfaces.</p>
In this study, an antiferritin/mixed-PEG coimmobilized soft surface was constructed onto polystyrene nanospheres, in order to solve the problems on conditional BSA blocking treatment. Though a nanosphere/antiferritin/mixed-PEG (LAmP) complex possessed the size and distribution similar with those of a nanosphere/antiferritin/BSA (LAB) complex, it showed a significantly higher immune response yield and a lower detection limit than the LAB complex in 100 % fetal bovine serum (FBS) solution, clearly demonstrating the usefulness of this PEGylation treatment in construction of efficient biodiagnosis systems.	
* Yuan xiaofei, Yoshimoto Keitaro and Nagasaki Yukio, <i>Anal. Chem. in press.</i>	
<b>References :</b>	
[1] Otsuka, H.; Nagasaki, Y.; Kataoka, K. <i>Biomacromolecules</i> <b>2000</b> , 1, 39. [2] Uchida, K.; Otsuka, H.; Kaneko, M.; Kataoka, K.; Nagasaki, Y. <i>Anal. Chem.</i> <b>2005</b> , 77, 1075. [3] Yuan, X.; Iijima, M.; Oishi, M.; Nagasaki, Y. <i>Langmuir</i> <b>2008</b> , 24, 6903.	

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**Presentation Title:**

Cytoplasmic Delivery of siRNA Based on the Polyion Complex with Cross-Linked Polyamine Nanogels Directed to Enhance the Gene Silencing Efficiency

**Abstract:**

RNA interference (RNAi) is a sequence specific posttranscriptional gene silencing pathway initiated by double strand small interfering RNA (siRNA) with 19 to 23 nucleotide base pairs, which induces endonucleolytic cleavage of complementary target mRNA. This powerful gene regulating method has a tremendous therapeutic potential on treating various intractable diseases including genetic disorders and cancer. Nevertheless, the naked siRNAs exhibit very low gene silencing efficiency *in vitro* and *in vivo* due to their poor intracellular uptake, low stability against enzymatic degradation in blood stream, and rapid clearance from renal glomeruli via systemic administration. To improve the efficiency of siRNA in both *in vitro* and *in vivo*, hydrophilic poly(ethylene glycol) (PEG)-polyamine block or graft copolymers were used for complexation with nucleic acid to form nano-sized PEGylated polyplexes composed of segregated polyion complex core surrounded by PEG palisade layers to increase biocompatibility and enzymatic tolerability. However, electrostatic interaction between siRNA and polyamine seems to be weak under extremely dilute conditions and high ionic strength conditions, because of the short base pairs of siRNA. In this study, PEGylated polyamine nanogels composed of nano-sized cross-linked poly(*N,N*-diethylaminoethyl)- methacrylate (PEAMA) gel and surrounding PEG palisade layers were evaluated as a new class of siRNA carrier to develop the PEGylated polyplex system (Figure 1). The cross-linked polyamine gel does not undergo dissociation and cleavage under the physiological condition, suggesting the PEGylated polyamine nanogel is potential siRNA carrier for the clinical use of siRNAs by systemic administration. Indeed, the nanogel/siRNA complex showed higher stability against polyanion exchange reaction than that of PEG-*b*-PEAMA/siRNA complex. Thus, the nanogel/siRNA complex promoted the cellular uptake of siRNA to HuH-7 (human hepatocarcinoma) cells compared with that of PEG-*b*-PEAMA/siRNA complex and naked siRNA, as determined by flow cytometry. Additionally, *in vitro* transfection study revealed that the specific gene silencing activities (RNAi activities) of siRNA were remarkably enhanced by nanogels/siRNA complexes compared with PEG-*b*-PEAMA/siRNA complexes. Therefore, the PEGylated polyamine nanogels would be utilized as a potential siRNA carrier for *in vivo* therapeutic application.

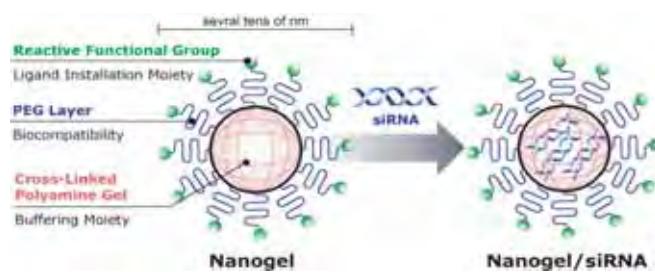


Figure 1. Schematic illustration of cross-linked polyamine nanogel and siRNA polyion complex.

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**Presentation Title:**

PEG-polyamine/DNA co-immobilized gold surfaces as a novel platform for DNA sensing: Comparison of PEG-*b*-polyamine layer and polyamine-*g*-PEG layer using XPS analysis

**Abstract:**

In order to establish high-performance DNA based sensors, it is important to design the functionalized surface that improves the orientation and density of the immobilized DNA on the surface. In our previous work, the immobilization of single-stranded DNA (ssDNA) with high densities and selective detection of the target ssDNA were accomplished by poly(ethylene glycol)-*block*-poly[2-(*N,N*-dimethylamino)ethyl methacrylate] (PEG-*b*-PAMA) modified gold surfaces<sup>1</sup>. In this study, to assess the function of PEG-*b*-PAMA modified gold surface (*Block-Surface*), comparative studies by surface plasmon resonance (SPR) and X-ray photoelectron spectroscopy (XPS) analyses with PAMA-*g*-PEG modified gold surface (*Graft-Surface*) were demonstrated.

The hybridization amounts of complementary (5'-GCTGGTGGC-3') and single-base mismatched ssDNA (5'-GCTGTTGGC-3') were evaluated by SPR sensor on the ssDNA (5'-dT<sub>20</sub>-GCCACCAGC-3')/polyamine-PEG co-immobilized gold surfaces. In the case of ssDNA immobilized *Graft-Surface*, there was no significant difference in the SPR angle shifts caused by the detection of complementary and mismatch ssDNA. On the other hand, the SPR angle shift caused by the detection of complementary ssDNA was six times higher than that of single-base mismatched ssDNA on ssDNA immobilized *Block-Surface*. In order to investigate the high-performance of ssDNA immobilized *Graft-Surface*, angle-dependent XPS analyses were carried out on the both polyamine-PEG modified gold surfaces. Figure 1 shows the changes in the atomic compositions ratio of Nitrogen/Carbon (N/C) by varying the take-off angle. In the case of *Block-Surface*, N/C ratio decreased with decrease in the take-off angle, indicating the localization of nitrogen element of PEG-*b*-PAMA near the gold surface was observed. In contrast, there was little change in the N/C ratio by varying the take-off angle on the *Graft-Surface*. These results indicated that the constructed PEG brush on *Block-Surface* was highly oriented manner compared to that on *Graft-Surface*. Thus, due to the construction of highly oriented PEG brush layer on the gold surface, the PEG/DNA co-immobilized surface prepared by PEG-PAMA block copolymer is anticipated to give high performance to the development of a useful platform for a DNA sensing and immobilization on gold surface.

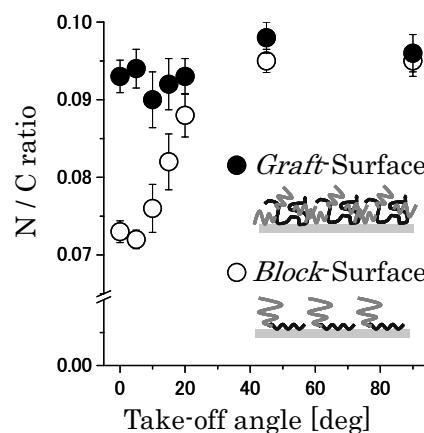


Figure 1. Changes in the atomic ratio of N/C obtained from angle-dependent XPS analysis by varying the take-off angle on (○) *Block-Surface* and (●) *Graft-Surface*. (n=3, S.D. shown as error bar).

**References :**

- 1) Yoshimoto K., Matsumoto S., Asakawa R., Uchida K., Ishii T., and Nagasaki Y., *Chem. Lett.* (2007) 36, 1444-1445.

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**Presentation Title:**

Modulation of lysozyme activity by smart copolymer PEAMA-g-PEG: Recovery of its enzymatic activity after heat treatment using polyion complex chemistry

**Abstract:**

Proteins have evolved to acquire highly specialized biological functions and are ideal for various applications in both medicinal chemistry and biotechnology<sup>1</sup>, though denaturation is one of major problems in protein chemistry. In this study, we show a novel technique for the regulation and preservation of enzymatic activity using a cationic smart copolymer, poly(*N,N*-diethylaminoethyl methacrylate)-graft-poly(ethylene glycol) (PEAMA-g-PEG), even after heat treatment at high temperature. The complex formation of lysozyme with PEAMA-g-PEG as shown in Figure 1, suppressed the enzymatic activity of lysozyme completely and outstandingly almost no conformational changes of the enzyme, indicating the complex formation and capping the active site of lysozyme by PEAMA-g-PEG despite the fact that both are positively charged macromolecule. It is known that nonionic polymer, PEG, can weakly interact with lysozyme<sup>2</sup> but the interaction between lysozyme and methacryloyl ended PEG (PEG-MA) had almost no effect on its enzymatic activity of lysozyme. Interestingly, the addition of an anionic polymer, poly(acrylic acid) (PAAc), recovered the inhibited enzymatic activity of lysozyme/PEAMA-g-PEG complex completely. To our surprise, even after heating of lysozyme with PEAMA-g-PEG for 20 min at 98 °C, the addition of PAAc recovered 80% enzymatic activity of lysozyme as shown in Figure 2. CD spectral analysis undoubtedly indicated that the irreversible inactivation of lysozyme induced by the heat treatment was extensively suppressed by the complex formation with PEAMA-g-PEG.

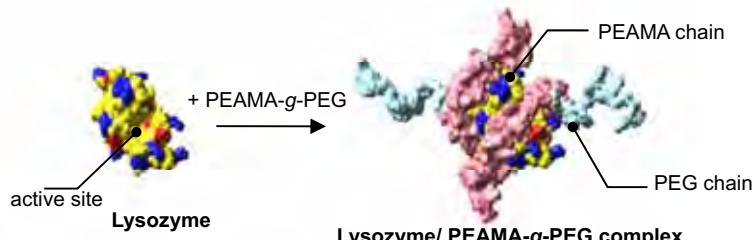


Figure 1. Schematic illustration for the complex formation of lysozyme with PEAMA-g-PEG. This graft copolymer caps the active site of lysozyme without any conformational change of lysozyme.

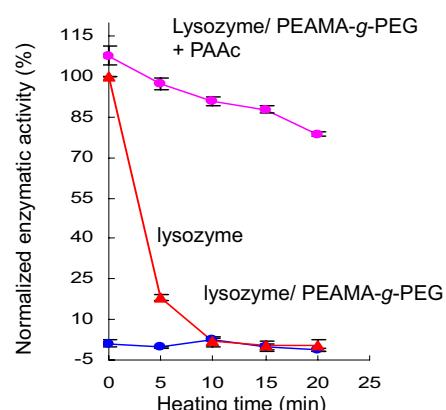


Figure 2. Changes in the enzymatic activity of lysozyme and the lysozyme/PEAMA-g-PEG complex as a function of the heating (98 °C) time.

**References :**

- [1] Heredia, K. L. *et al.* In situ preparation of protein-“smart” polymer conjugates with retention of bioactivity. *J. Am. Chem. Soc.*, (2005), 127, 16955.
- [2] Bloustein, J. *et al.* Light scattering and phase behaviour of lysozyme-poly(ethylene glycol) mixtures. *PRL*, (2006), 96, 087803.

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**Presentation Title:** Luminescence-based Colorimetric Discrimination of Single-nucleotide Transversions by the Combined Use of the Derivatives of DOTA-conjugated Naphthyridine and Its Terbium Complex

### Abstract:

Fluorescence-based detection technologies have often been applied in the field of DNA genotyping, due to their unique advantages in setting up sensitive and simple assays. Although they are regarded as effective approaches, there are still several problems, such as need for fluorophore-labeled DNA, the use of expensive enzymes, and the possibility of hybridization errors. In this study, we report a new type of genotyping method using naphthyridine (ND) derivatives and an abasic site-containing single stranded DNA (ssDNA). The abasic site is a location where hydrophobic microenvironments are provided for ligands to recognize nucleobases through hydrogen bonding<sup>1</sup>.

At the same excitation wavelength, ND-DOTA (**L**) which was newly designed showed the blue emission originated from naphthyridine moiety, while ND-DOTA-Tb (**L-Tb**) showed green emission based on an energy transfer from the naphthyridine moiety to Tb<sup>3+</sup>. From the experimental results by emission titration with the abasic site-containing DNA duplexes, the blue emission of **L** was selectively quenched by adding the abasic site-containing DNA duplexes that had pyrimidine bases opposite to the abasic site. In contrast, **L-Tb** showed the green metal-centered emission independently of bases opposite to the abasic site. Under optimized experimental conditions, a mixed solution containing **L** and **L-Tb** showed the pale blue emission and it can be used to analyze the purine-to-pyrimidine mutation sequences (R249S) of the cancer repression gene p53 with the naked eye as shown in Fig. 2(a). As is schematically illustrated in Fig. 2(b), when the mutation type ssDNA (**Y** = thymine (T)) was added to the mixed solution with the abasic site-containing ssDNA, the fluorescent color change from pale blue to green was observed under the UV lamp at a single excitation wavelength (the images of “DNA free” and “T” in Fig. 2(a)), while there was no change in the fluorescence color when the wild type ssDNA (**Y** = guanine (G)) was added to the mixed solution with the abasic site-containing ssDNA (the images of “DNA free” and “G” in Fig. 2(a)). The color change showed clearly that the mixed solution containing **L** and **L-Tb** with an abasic site-containing ssDNA enabled to the luminescence-based colorimetric discrimination of single-nucleotide transversions with the naked eye at a single excitation wavelength without the enzymes and fluorophore-labeled DNAs.

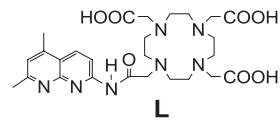


Fig. 1 Chemical structure of **L**

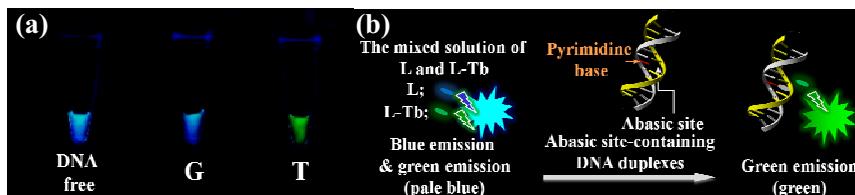


Fig. 2 (a) Fluorescence image and (b) schematic illustration of the colorimetric discrimination of single nucleotide transversion (R249S) using the mixed solution containing **L** and **L-Tb** in the presence and absence of the abasic site-containing DNA duplexes (5'-GGTGAGGATGGG~~X~~CTCCGGTTCATG-3'/5'-CATGAACCGGAG~~Y~~CCCATCCTCAC-3'; ~~X~~ = abasic site, left to right: DNA free, **Y** = G and T).

### Reference:

[1] K. Yoshimoto, S. Nishizawa, M. Minagawa, and N. Teramae, *J. Am. Chem. Soc.* Vol. 125 (2003) 8982.

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**Presentation Title:**

Effects of Mixed-Poly(ethylene glycol) Tethered Chain Layer on Activity of Fab' Fragment on a Gold Sensor Surface

**Abstract:**

In order to improve both an antigen binding activity and a nonfouling property of antibody-immobilized gold sensor surface, mixed-PEG<sup>1</sup> tethered chain was successfully constructed on anti-C reactive protein (CRP) Fab' fragments preimmobilized gold sensor surface. The constructed Fab'/mixed-PEG co-immobilized gold sensor surfaces were characterized by surface plasmon resonance (SPR) analyzer, <sup>125</sup>I radiometric assay.

As shown in Figure 1, the SPR responses caused by the injection of CRP on the Fab'/mixed-PEG co-immobilized surface decreased significantly with time when Fab' fragments on the surface was stood for 0-60 min prior to PEGylation (open circle). On the contrary, when the Fab' fragments immobilized gold surface was treated immediately upon preparation with the mixed-PEG, a fairly high SPR responses of CRP was retained (closed circle). From <sup>125</sup>I radiometric assay (data not shown), it was confirmed that no desorption of Fab' fragments from the surfaces during standing processes for 0-60 min before and after PEGylation was observed. These results indicated that the mixed-PEG tethered chains, which fill the interstices on Fab' fragments preimmobilized gold sensor surface, prevented the inactivation of Fab' fragments effectively. This new insight provides important guidelines for the construction of high-performance antigen immobilized gold sensor surfaces.

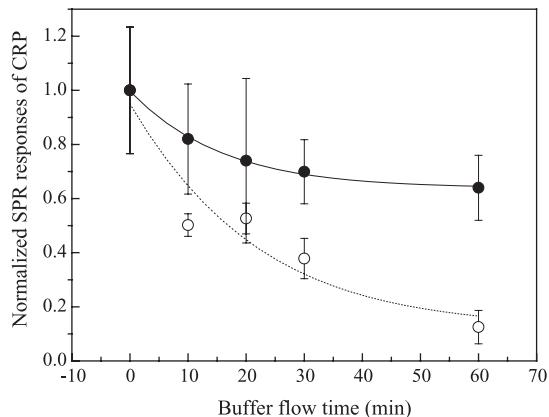


Figure 1. Normalized SPR responses caused by the injection of 1  $\mu$ M CRP on the Fab'/mixed-PEG co-immobilized surfaces under the condition of buffer flow before (open circle) and after (closed circle) PEGylation as a function of flow time. SPR measurements were carried out at a constant flow rate of 5  $\mu$ L/min at 25 °C. (n = 4,  $\pm$  SEM).

**References:**

- 1) Uchida K., Otsuka H., Kaneko M., Kataoka K., Nagasaki Y., Anal. Chem. 77 (2005) 1075-1080.

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<b>Presentation Title:</b> Cross-linked Polymer Micelles with Biodegradable Ionic Cores for Drug Delivery	
<p><b>Abstract:</b></p> <p>Intramicellar cross-linking is one of the promising methods to improve the stability of polymeric micelles. In particular, cross-linkers with disulfide linkages can be used for potential drug delivery applications because the intracellular environment is more reductive than the extracellular fluid, which would result in a considerable difference in the cleavage rate of disulfide bonds between the intracellular and extracellular compartments. In this study, polymer micelles with biodegradable cross-links in the core were explored as drug carriers for chemotherapeutic agents. Block ionomer complexes of poly(ethylene oxide)-<i>b</i>-poly(methacrylic acid) (PEO-<i>b</i>-PMA) and divalent metal cations (Ca<sup>2+</sup>) were utilized as templates for the synthesis of cross-linked micelles(1,2). Cross-linked micelles with different degrees of cross-linking were synthesized via 1) condensation of PEO-<i>b</i>-PMA copolymers by Ca<sup>2+</sup> into spherical micelles of core-shell morphology and 2) cross-linking by using cystamine as a biodegradable cross-linker. Doxorubicin or cisplatin was loaded into the cross-linked core of polymeric micelles. The physicochemical properties, loading efficacy as well as the release of anticancer drug from the micelles were studied. Biodegradable disulfide bonds were incorporated into the micellar cross-linked core using cystamine as a cross-linker. The resulting cross-linked micelles represented hydrophilic nanospheres of core-shell morphology. The ionic PMA core of the micelles showed pH-dependent swelling behavior and allowed for the encapsulation of doxorubicin and cisplatin. Incubation with 10mM glutathione had shown a remarkable fast release of drug from cystamine cross-linked micelles due to the cleavage of disulfide bonds in the ionic core. Polymer micelles of nanoscale size with biodegradable cross-links in ionic cores could facilitate drug release under intracellular redox conditions. These novel biodegradable cross-linked micelles are expected to be attractive nanocarriers for delivery of anticancer drugs.</p>	
<p><b>References:</b></p> <ol style="list-style-type: none"> <li>1. Bronich, T.K., Keifer, P.A., Shlyakhtenko, L.S., Kabanov, A.V. <i>J Am. Chem. Soc.</i> 127 (2005) 8236-8237.</li> <li>2. Bontha, S., Kabanov, A.V., Bronich, T.K. <i>J. Controlled Rel.</i> 114 (2006) 163-174.</li> </ol>	

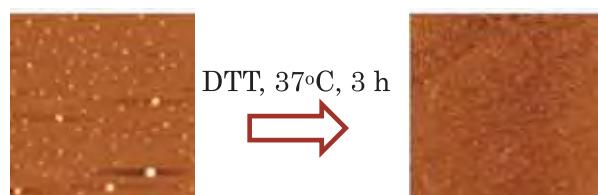


Fig. 1 Degradation of *cl*PEO-*b*-PMA micelles in the presence of dithiothreitol (DTT)

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Atom-scale and Mesoscale Infrared Plasmonic Materials

**Abstract:**

The spectral range and dispersion relation of plasmon drastically change as the material reduces its dimensionality and changes its shape. Recently, we have clarified that infrared plasmons with small phase/group velocities are confined and propagates in ultimately tiny systems such as atom sheets and atom chains that are supported on the dielectric media with electrical isolation to these tiny metal objects[1-4]. While the electron scattering spectroscopy with highly collimated low-energy electrons was successfully used to determine the dispersion relation and the linewidth of the infrared plasmons, we still lack in knowing how they appear in optical spectroscopy.

We have performed *in situ* electron scattering spectroscopy of infrared plasmonic materials such as metallic atom chains and atom sheets in ultrahigh vacuum condition. Also, we performed *in situ* IR spectroscopy of atom chains in UHV as well as nanofilms grown in aqueous solution which showed dramatic enhancement in the vibrational signal of adsorbed organic monolayers[5]. While electron spectroscopy offers extreme sensitivity to the atom-scale objects and longitudinal dielectric constants, IR spectroscopy gives access to the objects with very rough nanomorphology and transverse dielectric constants. So the two methods can be combined in a complementary manner.

**References:**

- [1] T. Nagao, et al., proc. SPIE **6641**, 664116(2007).
- [2] T. Nagao et al., Phys. Rev. Lett. **97**, 116802 (2006).
- [3] C. Liu et al., Phys. Rev. B **77**, 205415 (2008).
- [4] C. Liu et al., Nanotechnology **19**, 355204 (2008).
- [5] D. Enders et al., Jpn. J. Appl. Phys. **49** (Express Letters), L1222-1224 (2007).

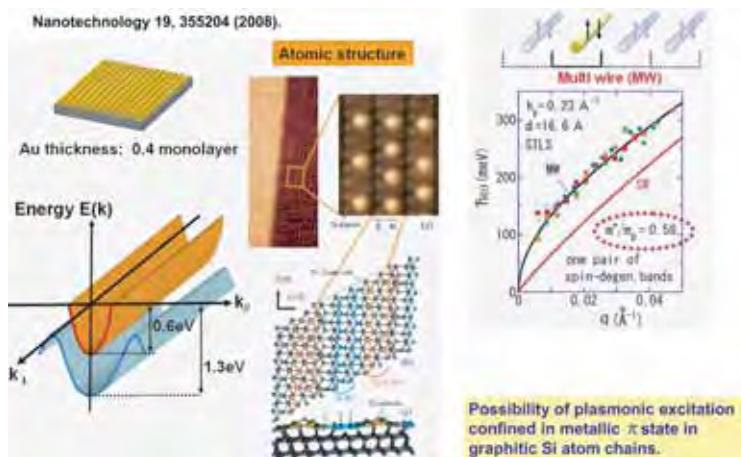
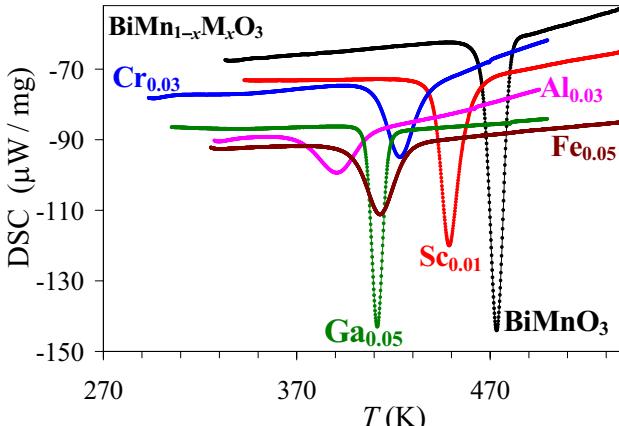
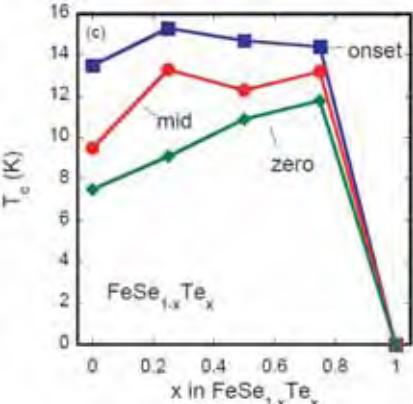
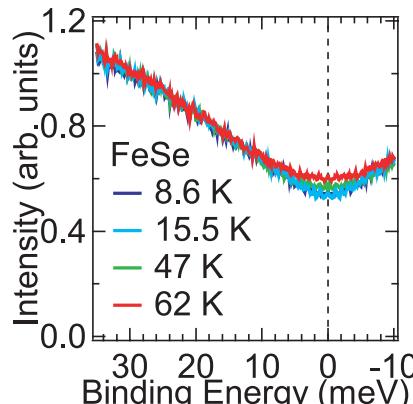


Fig. 1: Left side: Schematics of the atomic structure and the electronic structure of the Au atom chains on the silicon surface. Right side: Plasmon dispersion of the atom chains measured by low-energy electron scattering spectroscopy.

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<b>Presentation Title:</b> Effects of cation and oxygen doping on structural, physical, and chemical properties of multiferroic $\text{BiMnO}_3$ and $\text{BiCrO}_3$	
<b>Abstract:</b> <p>Mutriferroics are an interesting class of materials from viewpoints of application and basic physics. <math>\text{BiMnO}_3</math> has been extensively studied as a multiferroic material. Heterovalent substitutions in the Bi sublattice of <math>\text{BiMnO}_3</math> have been investigated in a number of works. Transitions with different spin, charge, and orbital orders were found in <math>\text{Bi}_{1-x}\text{M}_x\text{MnO}_3</math> (<math>\text{M} = \text{Ca}</math> and <math>\text{Sr}</math>). There is very limited information on oxygen content and isovalent substitution effects in <math>\text{BiMnO}_3</math>. In this presentation, we will show results of investigation of effects of oxygen content and isovalent substitutions in the Mn(Cr)- and Bi-sublattices of <math>\text{BiMnO}_3</math> and <math>\text{BiCrO}_3</math> on the magnetic, structural, and thermal properties. All the samples were prepared at high pressure of 6 GPa and 1333-1453 K. Phase diagrams in the whole compositional range were constructed for <math>\text{BiMn}_{1-x}\text{Sc}_x\text{O}_3</math> [1], <math>\text{BiMn}_{1-x}\text{Cr}_x\text{O}_3</math>, <math>\text{Bi}_{1-x}\text{La}_x\text{MnO}_3</math>, and <math>\text{Bi}_{1-x}\text{Y}_x\text{MnO}_3</math>, and <math>\text{Bi}_{1-x}\text{Y}_x\text{CrO}_3</math>. The orbital order of <math>\text{BiMnO}_3</math> was found to be very fragile, and the temperature of orbital ordering is very sensitive to substitutions in the Mn sublattice (Figure 1) [2]. The ferromagnetic temperature in the orbital-ordered state is only slightly affected. Ferromagnetic cluster-glass behavior and re-entrance spin-glass transitions were found in the orbital-disordered state [3]. In <math>\text{BiMn}_{1-x}\text{Sc}_x\text{O}_3</math> and <math>\text{BiMn}_{1-x}\text{Cr}_x\text{O}_3</math>, the monoclinic phases are formed in the whole compositional range. In <math>\text{Bi}_{1-x}\text{Y}_x\text{MnO}_3</math> and <math>\text{Bi}_{1-x}\text{Y}_x\text{CrO}_3</math>, the orthorhombic <math>\text{GdFeO}_3</math>-type phase is stabilized at <math>x = 0.05-0.10</math>. The oxygen content has effects similar to those of <math>\text{BiMn}_{1-x}\text{Sc}_x\text{O}_3</math>. However, new superstructures were found in <math>\text{BiMnO}_{3+\delta}</math>.</p>	
	<p>Figure 1. Effect of isovalent substitutions in the Mn-sublattice of <math>\text{BiMnO}_3</math> on the orbital-ordering transition temperature [2].</p>
<b>References:</b>	
[1] A.A. Belik, T. Yokosawa, K. Kimoto, Y. Matsui, E. Takayama-Muromachi, <i>Chemistry of Materials</i> 19, 1679-1689, 2007.	
[2] A.A. Belik, E. Takayama-Muromachi, <i>Inorganic Chemistry</i> 46, 5585-5590, 2007.	
[3] A.A. Belik, E. Takayama-Muromachi, <i>Journal of Physics: Condensed Matter</i> 20, 025211, 2008.	

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<b>Presentation Title:</b> Highly Crystalline and Active Nanoporous Metallosilicate Nanocages	
<b>Abstract:</b> <p>Mesoporous silica materials discovered by Mobil researchers have received much attention in the recent years because of their application in various fields such as catalysis, adsorption and separation, and nanodevices.<sup>1-4</sup> However, these materials are amorphous in nature and lack acidity, which is not suitable for acid catalyzed reactions. Here we aim to fabricate mesoporous materials with crystalline wall structure, which are expected to provide a lot of acid sites. Highly ordered crystalline mesoporous titano and zinc silicate materials with excellent textural properties were successfully synthesized for the first time with amphiphilic surfactant [3-(trimethoxysilyl)propyl] hexadecyldimethylammonium chloride as a structure directing agent under hydrothermal synthesis condition at 150 °C via rotating mode. The materials were thoroughly characterized by powder XRD, HR-FESEM and nitrogen adsorption isotherms. Both the samples show a peak at lower angle which is a typical characteristic of a well ordered mesoporous structure, and several peaks at higher angle, suggesting that the samples are highly crystalline in terms of both the order of the pores and the atoms (not shown). Well-ordered rectangular shaped crystals with uniform size, which are similar to that of microporous titanosilicates (TS-1), are clearly seen in the sample (Fig. 1). Similar well ordered crystals are observed for zinc silicates. The textural parameters of the samples have also been studied. It is found that both titano and zinc silicate samples exhibit the surface area of ca. 500 m<sup>2</sup>/g and large pore volume. Moreover, the catalytic activity of the materials has been evaluated on several acid catalyzed reactions. The detailed results will be discussed during the presentation.</p>	 S4800 10.0kV 8.3mm x9.00k SE(U) 5.00um
<b>References:</b> K. Ariga, A. Vinu*, Q. Ji, O. Ohmori, J. Hill, S. Acharya, J. Koike, S. Shiratori, "Angew. Chem. Int. Ed.", 47, 7254-7257 (2008). A. Vinu*, Adv. Funct. Mater. 18, 816-827 (2008) P. Srinivasu, S. Alam, V.V. Balasubramanian, S. Velmathi, D.P. Sawant, W. Bohlmann, S.P. Mirajkar, K. Ariga, S.B. Halligudi, A. Vinu*, Adv. Funct. Mater. 18, 640-651 (2008) D.P. Sawant, J. Justus, V.V. Balasubramanian, K. Ariga, P. Srinivasu, S. Velmathi, S.B. Halligudi, A. Vinu*, "Chem. Euro. J.", 14, 3200-3212 (2008).	

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<b>Home Page:</b>	
<b>Presentation Title:</b> Superconductivity of FeSe and related compounds	
<b>Abstract:</b> The discovery of the iron-based superconductors stimulated huge number of researchers. After the first report [1], more than 500 papers had been reported within this one year. Many of them were focused on the exploration of new materials with higher superconducting transition temperature ( $T_c$ ). Nowadays, those materials can be categorized into four groups from structural point of view. FeSe has the simplest structure among the iron-based superconductors. This fact implies the advantage for studying the essential feature of the iron-based superconductors.	
	Fig. 1 Substitution dependence of $T_c$ of $\text{FeSe}_{1-x}\text{Te}_x$ [4]
	
	Fig. 2 Symmetrized photoemission spectra of FeSe
<b>References:</b>	<ul style="list-style-type: none"> <li>[1] Y. Kamihara, T. Watanabe, M. Hirano, H. Hosono, JACS <b>130</b> (2008).</li> <li>[2] Y. Mizuguchi, F. Tomioka, S. Tsuda, T. Yamaguchi, Y. Takano, APL <b>93</b> 152505 (2008).</li> <li>[3] Y. Mizuguchi, F. Tomioka, S. Tsuda, T. Yamaguchi, Y. Takano, APL <b>94</b> 012503 (2009).</li> <li>[4] Y. Mizuguchi, F. Tomioka, S. Tsuda, T. Yamaguchi, Y. Takano, cond-mat/080.1123.</li> </ul>

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<b>Presentation Title:</b> A graphene-based double quantum-dot system	
<p><b>Abstract:</b>            The recent discovery of single- and few-layers graphene (FLG) has opened a door to a new area of low-dimensional physics [1]. The low-energy physics of graphene is described theoretically by (2+1)-dimension. Dirac fermion, which leads to rich physics inherited from quantum electrodynamics (QED). From the application point of view, the ballistic transport and high mobility in graphene and FLG make it possible candidate for future nano-electronic quantum devices.</p> <p>Here, we present the first demonstration of a graphene-based double quantum-dot system, which exhibits single-electron transport on two lateral quantum dots coupled in series. Coupled quantum-dot systems have been proposed for various applications as new logic and architecture, such as quantum computation and quantum cellular automata. Our results suggest an important step for the realization of integrated quantum devices in graphene electronics.</p> <p>Graphene and FLG samples are prepared by micromechanical cleavage of graphite crystals and deposited on the surface of a Si substrate with a 300 nm thickness of oxidized silicon. Optical microscope contrast and Raman spectroscopy measurements can be identified the single-, double- and few-layer graphene flakes on the substrate. Graphene nanostructures can be fabricated by carving out of the graphene sheet. By using high-resolution electron-beam lithography, we patterned a thin ZEP resist that protected chosen areas during oxygen plasma etching and allowed us to carve graphene into a desired geometry. Figure 1 shows one of our working graphene devices. The devices consisted of two isolated island as quantum dots, connected via two short constrictions to wide source and drain regions. Three lateral graphene side gates have been fabricated close to the active graphene structure. Quantum dots are designed in a triangular shape (the area <math>S \approx 0.005 \mu\text{m}^2</math>), and the constrictions were equal length and width of about 15 nm. In the presentation, the details on the electron transport characteristics on the graphene-based coupled quantum dots will be reported.</p>	

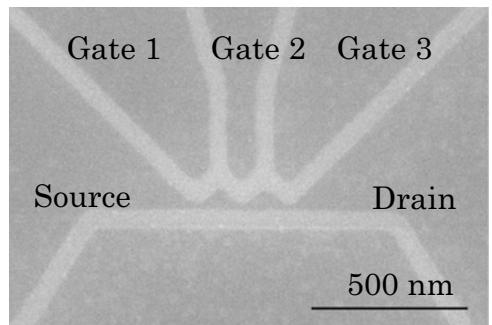
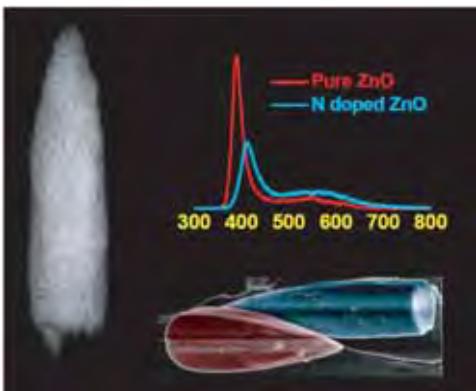
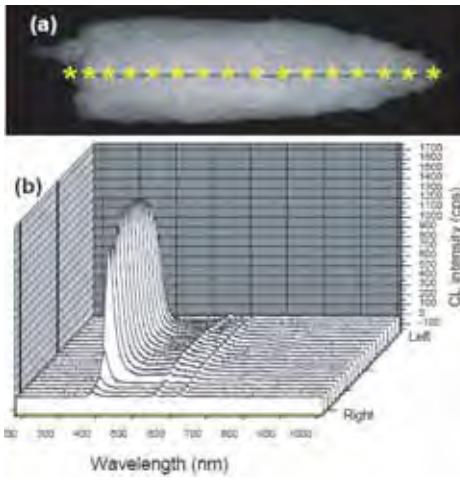
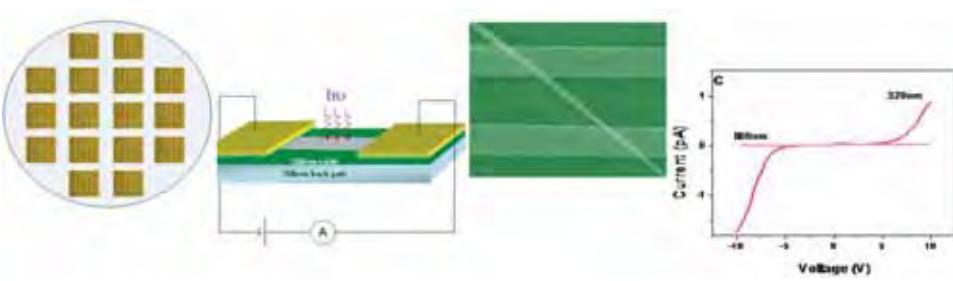
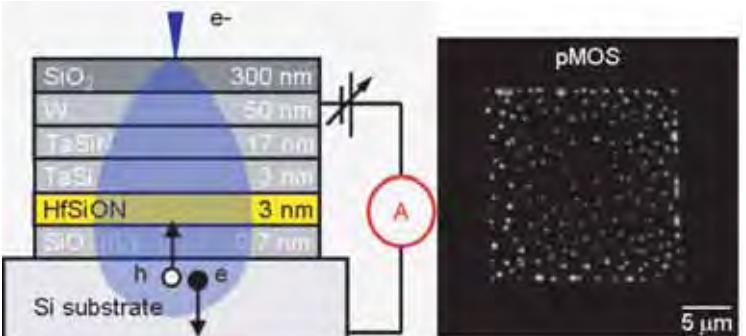


Figure 1: Scanning electron microscope image of the measured device with electrode assignment.

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<b>Presentation Title:</b> Solution Synthesis, Cathodoluminescence, and Field-Emission Properties N-Doped ZnO Nanobullets	
<b>Abstract:</b> <p>In the absence of external influences, homogenous crystallization in solution is expected to lead to growth that is symmetric at least in two opposite facets. Such was not the case when we synthesized ZnO nanostructures by employing a solvothermal technique. Instead, the reaction product was found to consist of tiny bullet-shaped single crystals with abrupt hexagonal bases and sharp tips. A careful analysis of the product and the intermediate states of the synthesis reveals that one of the reaction intermediates with sheet-like morphology acts as a self-sacrificing template and induces such unexpected and novel growth. The synthesis was further extended to dope the nanobullets with nitrogen as previous studies showed this can induce p-type behavior in ZnO, which is technologically complementary to the naturally occurring n-type ZnO. Herein, a soft-chemical approach is used for the first time for this purpose, which is otherwise accomplished only with high-temperature techniques. Investigations using cathodoluminescence (CL) spectroscopy reveal stable optical behavior within a pure nanobullet, while the CL spectra from the surfaces and the cores of the doped samples are different, pointing at a N-rich core. Finally, even though N-doped ZnO is known to have high conductivity, our study demonstrates that the field-emission characteristics of ZnO can also be largely enhanced by means of N doping.</p>	
 	
<b>References :</b> U. K. Gautam, L. S. Panchakarla, B. Dierre, X. Fang, Y. Bando, T. Sekiguchi, A. Govindaraj, D. Golberg, C. N. R. Rao, <i>Adv. Funct. Mater.</i> (in press) <a href="https://doi.org/10.1002/adfm.200801259">10.1002/adfm.200801259</a>	

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<b>Presentation Title:</b> One-Dimensional (1D) Semiconductor ZnS Nanostructures -- Novel Functional Materials	
<p><b>Abstract:</b>            Zinc sulfide (ZnS), is one of the first semiconductors discovered and one of the most important materials in the electronics with a wide range of applications, including LEDs, electroluminescence, flat panel displays, infrared windows, sensors, lasers, and biology etc [1,2].</p> <p>In this presentation, we will not only present the new method to control the growth of 1D ZnS nanostructures, such as temperature-controlled growth, shape- and size-controlled growth, their arrays and hierarchical nanostructures [3]. But also we will introduce our latest progresses on the exploration of 1D ZnS nanostructure as excellent and potential field-emitters and ultraviolet (UV) sensors and lasers [4,5]. For example, crystal orientation-ordered ZnS nanobelt quasi-arrays were fabricated using a non-catalytic and template-free thermal evaporation process, and field-emission measurements show that these novel arrays are decent field emitters possessing a current density more than 20 times higher than that of randomly-oriented ZnS nanobelt ensembles at a macroscopic field of <math>5.5 \text{ V/}\mu\text{m}</math> [6]. Individual ZnS nanobelt-based visible-blind UV sensors fabricated and characterized for the first time. The photoresponsivity of a novel individual ZnS nanobelt-based UV sensor exhibits over three orders of the enhancement being illuminated by a UV light compared to a visible light etc.</p>	
 <p>The figure consists of four panels. The first panel is a circular inset showing a 4x4 grid of yellow ZnS nanobelts. The second panel is a cross-sectional diagram of the sensor structure, showing a green nanobelt layer on a substrate with a blue insulating layer. The third panel is a photograph of a green nanobelt array. The fourth panel is a graph of Current (nA) versus Voltage (V). The graph shows a sharp increase in current at approximately -5V, with a peak current of about 8 nA labeled 'Holes'. At 320nm UV illumination, the current increases to approximately 100 nA, labeled '320nm'.</p>	
<p>Figure an individual ZnS nanobelt-based UV sensor</p>	
<p><b>Acknowledgement:</b>            This work was financially supported by the World Premier International Research Center on Materials Nanoarchitectonics (MANA), MEXT, tenable at NIMS, Japan.</p>	
<p><b>References:</b></p> <p>[1] X. S. Fang et al J. Mater. Chem. 18, 509 (2008); J. Mater. Sci. Technol. 22, 721 (2006); Adv. Funct. Mater. 15, 63 (2005); J. Phys. Chem. C. 111, 8469 (2007); Nano Letters. 8, 2794 (2008); Adv. Mater. 19, 2593 (2007); Chem. Commun. 3048 (2007); J. Phys. Chem. C. 112, 4735 (2008).</p>	

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<b>Presentation Title:</b> A versatile application of electron-beam-induced current technique in semiconductor diagnosis	
<b>Abstract:</b> We presented advanced semiconductor diagnosis by using electron-beam-induced current (EBIC) technique. By varying the parameters such as temperature, accelerating voltage, bias voltage, and time, it is possible to extend EBIC application from conventional defect characterization to advanced device diagnosis. Since electron beam can excite a certain volume even it is beneath the surface passive layer, EBIC can sometimes very easy to diagnose complicated devices with hybrid structure.	
Three topics were selected to demonstrate EBIC applications.[1] First, the electrical recombination activities of grain boundaries and their interaction with Fe impurity in photovoltaic multicrystalline Si are clarified by temperature-dependent EBIC. Second, the detection of dislocations between strained-Si and SiGe virtual substrate are shown to overcome the limitation of depletion region. Third, the observation of leakage sites in high-k gate dielectric is demonstrated for the characterization of advanced hybrid device structures. Fig.1 illustrated the application of EBIC on the next generation CMOS device with high-k/metal gate structure. Local leakage sites in the gate dielectric can be directly visualized without peeling off covering layers and electrodes.	
For prospect, it is optimistic to image that this multi-dimensional EBIC technique will be quite helpful for studying novel materials and devices in future semiconductor research.	Fig. 1 Right: Illustration of EBIC on MOS with high-k/metal gate. Left: Top-view EBIC image of leakage sites in pMOS.
<b>References:</b>	
[1] J. Chen, X. Yuan, T. Sekiguchi, Scanning 30 (2008) 347-353.	

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**Home Page:****Presentation Title:**

Fabrication of oriented oxide films by pulsed laser deposition using two-dimensional inorganic nanosheet as a seed layer

**Abstract:**

The control of deposited films is one of the most important issues in thin film fabrication. Since the growth of films is strongly dominated by the surface structure of the substrate, one effective and feasible way is to use seed layers to introduce desired atomic regularity to the surface. Recently, two-dimensional crystals called "nanosheet" have been synthesized via delamination of various layered compounds. Nanosheets have notably high two-dimensional anisotropy with an ultrathin thickness of around 1 nm and a lateral size of up to several tens of micrometers. Using this unique two-dimensional material, novel method to control the orientation of sol-gel deposited films has been developed. [1]

In this study, we tried to apply this technique to a film fabrication via dry-process.  $\text{SrTiO}_3$  was deposited onto a highly organized monolayer film of a perovskite-related nanosheet ( $\text{Ca}_2\text{Nb}_3\text{O}_{10}$  nanosheet) by pulsed laser deposition, and succeeded to fabricate well crystallized (100) oriented films. The deposited films were characterized by XRD and TEM (Fig.1). Well oriented film growth of  $\text{TiO}_2$  (001) was also succeeded on the nanosheet seed layer substrate, demonstrating wide applicability of this method.

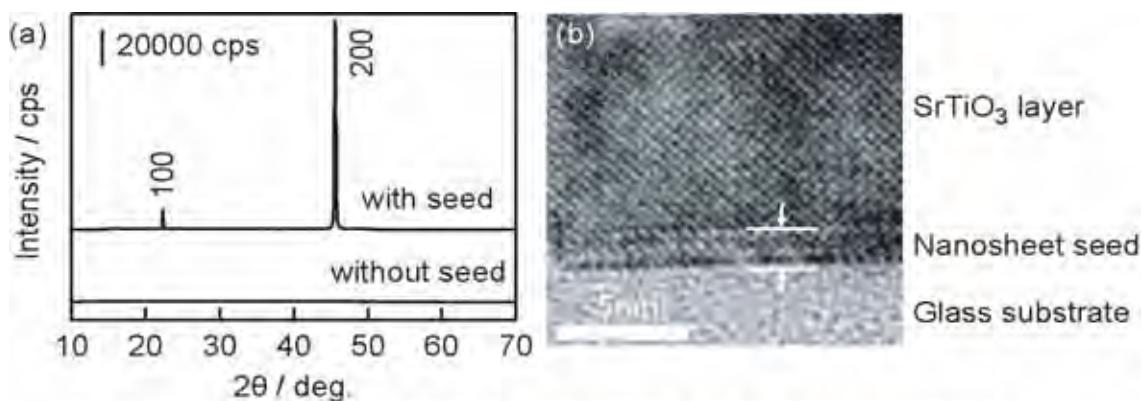
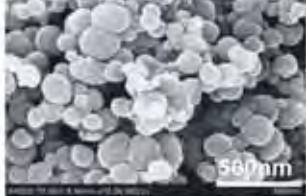
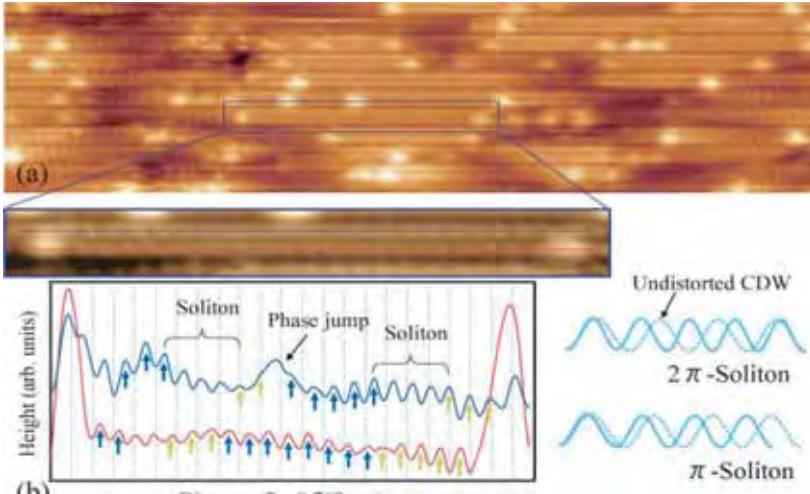


Figure 1(a) XRD patterns for  $\text{SrTiO}_3$  thin films, and (b) cross-sectional TEM image for (100) oriented  $\text{SrTiO}_3$  film.

**References:**

[1] T. Shibata et al., Adv. Mater. 20, 231 (2008).

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<b>Presentation Title:</b> Development of Ordered Nanoporous Materials for Electrochemical Applications	
<b>Abstract:</b> <p>Ordered nanoporous carbon materials are potentially of great technological interest for the development of electronic, catalytic, hydrogen-storage systems and adsorption of biomolecules [1-2]. The textural parameters of the nanoporous carbon materials are critical in many industrial applications particularly, separation, adsorption and fuel cells. However, a little attention has been given in the studies to the textural parameters control of nanoporous carbon materials. The present study is focused on the preparation ordered nanoporous carbon using a small organic molecule namely glucose as a carbon source.</p>	   
	Fig: HRSEM and TEM images of MCG-1.0 material
	<p>The nanoporous carbons were prepared using MCM-48 as a template and samples are designated as MCG-x where x denotes the glucose to template weight ratio. These materials possess well ordered structure with regular particle size (Fig.). The specific pore volume is in the range of 0.93-1.51 cm<sup>3</sup>/g and pore diameter in the range of 1.6-2.3 nm. The specific surface of MCG-0.75 is 1384 m<sup>2</sup>/g and increases to 2073 m<sup>2</sup>/g for MCG-1.0, which is higher than nanoporous carbons prepared using sucrose as a carbon source. These exciting results indicate that the carbon source with a small molecular size is critical to achieve the nanoporous carbon materials with excellent textural characteristics. These results indicate that the textural parameters of nanoporous carbon samples can be finely controlled using glucose as a carbon source. In addition, the electro catalytic activity of MCG materials has been studied. It has been found that the electric double layer capacitance is dependent on weight% of Pt loaded and textural parameters of MCG materials. It has been found that MCG shows superior performance compared with carbon black due to its large ordered pore channels which are continuous connected with the large quantity of small pores in the carbon pore walls.</p>
<b>References:</b>	
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<b>Presentation Title:</b> Phase modulation of quasi-one-dimensional charge-density waves induced by impurities	
<b>Abstract:</b> <p>Low-dimensional materials attract strong research interests because of their fascinating properties due to size reduction and their promising for future applications. Being cooled to a critical temperature, pure low-dimensional metals generally undergo a Peierls transition, which leads to the formation of charge-density waves (CDW) accompanied by a periodic lattice distortion through electron-phonon coupling. Impurities play an important part in determining both static and dynamic CDW properties through scattering electrons, which modifies both phase and amplitude of the CDW state. Especially, the phase pinning of CDW due to interaction with impurities is a central concept for explaining various phenomena including nonlinear conductivity and narrow band noise [1]. This issue, however, remains to be fully understood in spite of enormous theoretical and experimental studies, partly because of the absence of direct observation of the phase modulation in real space.</p>	 <p>Figure (a) shows an STM image of Co adatoms (bright protrusions) adsorbed on a Si(111)-4x1-In surface. The image reveals a periodic lattice distortion. Figure (b) shows line profiles taken along the lines indicated in (a), illustrating the CDW phase modulations. The profiles show a periodic oscillation with arrows indicating phase jumps. To the right, three schematic diagrams illustrate different phase modulations: 'Undistorted CDW' (a smooth sine wave), '2π-Soliton' (a sine wave with a phase jump of <math>2\pi</math>), and 'π-Soliton' (a sine wave with a phase jump of <math>\pi</math>).</p>
<p>Fig. (a) STM image of Co adatoms (bright protrusions) adsorbed Si(111)-4x1-In surface taken at -1.2 V. (b) Line profiles taken of the lines indicated in (a), showing CDW phase modulations as arrows indicate.</p>	
<p>A self-organized array of In atomic wires, the Si(111)-4x1-In surface, provides the opportunity of such direct observation as it exhibits the quasi-one-dimensional (Q1D) CDW transition [2,3], as long as scanning tunneling microscopy (STM) is applied. By adding very small amount of Co adsorbates (~0.02 ML) onto the In atomic wires and with STM performed at 80 K, we succeeded in obtaining direct images of the phase and amplitude modulation of CDW due to the emergence of Co adatoms. Concepts of phase pinning, phase slip and phase fluctuation are used to interpret the observed phase modulation that shows a strong bias dependence. Our observation discovers some new defect effects on the CDW that have not been reported yet.</p>	
<b>References:</b>	
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[3] C. Liu, T. Uchihashi, and T. Nakayama, Phys. Rev. Lett. <b>101</b> , 145104 (2008).	

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<b>Presentation Title:</b> Deep-ultraviolet Diamond-based Photodetector for high-power excimer lamp	
<p><b>Abstract:</b>            The next generation photolithography system, which uses a stepper with an excimer laser such as an ArF laser (<math>\lambda=193\text{nm}</math>) and an F2 laser (<math>\lambda=157\text{nm}</math>), requires deep-ultraviolet (DUV) detection. Currently, Si-based photodetectors are primarily used to detect UV light. However, they require filters to stop energy photons from visible and infrared light and have low efficiency. In addition, they easily degrade by the UV light. Diamond-based photodetector is a promising candidate for UV and DUV detection and overcome these limitations. In order to achieve and demonstrate diamond-based photodetector for UV and DUV detection, we fabricated Schottky barrier photodiode (SPD) with the vertical-type by using heavily B-doped p<sup>+</sup>-diamond (100) substrates.         </p> <p>The p-diamond epilayers were homoepitaxially grown by microwave plasma chemical vapor deposition (MPCVD) on the heavily B-doped p<sup>+</sup>-diamond (100) substrates commercialized by Technological Institute for Super-hard and Novel Carbon Materials (TISNCM). The substrate was <math>2.5 \times 2.5 \times 0.5 \text{ mm}^3</math> in size, and the B concentration ([B]) was measured to be around <math>1 \times 10^{20} \text{ cm}^{-3}</math> by secondary-ion mass spectroscopy (SIMS). The unintentionally B-doped p-diamond epilayers with [B] in the range <math>10^{15}</math> to <math>10^{16} \text{ cm}^{-3}</math> analyzed by SIMS were grown by CH<sub>4</sub> and H<sub>2</sub> gases. The ratio of CH<sub>4</sub> to H<sub>2</sub> was 0.08 %, and the corresponding flow rates of CH<sub>4</sub> and H<sub>2</sub> were 0.4 and 500 sccm, respectively. The reactor pressure was fixed at 106 hPa during growth. The growth was performed at <math>\sim 800 \text{ }^\circ\text{C}</math>. The thickness of epilayer was about 0.5 <math>\mu\text{m}</math>. To obtain Ohmic contact, Ti (40 nm)/ WC (30 nm) films were deposited on the back-side of the diamond substrate, subsequently annealed at 600 <math>^\circ\text{C}</math> for 1 h in an argon ambient. The semitransparent WC Schottky contact was deposited on the defined circle patterns on the diamond epilayer by a photolithographic technique. The diameter of WC Schottky contact was 1 mm.         </p> <p>Figure 1 shows a dark current and photocurrent under 220-nm light illumination as a function of applied voltage. Here, the forward voltage and the reverse voltage correspond to positive and negative biases, respectively. The reverse leakage current of the SPD is smaller than the detection limit of <math>10^{-14} \text{ A}</math>. The rectification ratio is determined to be around <math>10^{12}</math> at <math>\pm 3 \text{ V}</math>. The ideality factor (n value) of the SPD is 1.1, and the Schottky barrier height is determined to be <math>1.42 \pm 0.01 \text{ eV}</math>. The SPD is operated in only the reverse bias mode. The photocurrent is almost constant with increasing the reverse bias voltage.</p>	
<b>References:</b>	
*M. Imura, M. Y. Liao, J. Alvarez, and Y. Koide "Schottky-Barrier Photodiode using p-Diamond Epilayer Grown on p+-Diamond Substrate": Diamond & Related Materials, (In press). *M. Imura, M. Y. Liao, J. Alvarez, and Y. Koide "Vertical-type Schottky-Barrier Photodiode using p-Diamond Epilayer Grown on Heavily Boron-doped p+-Diamond Substrate": Diamond & Related Materials, 17 (2008) 1916-1921.	

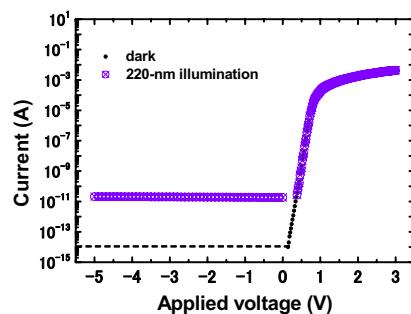
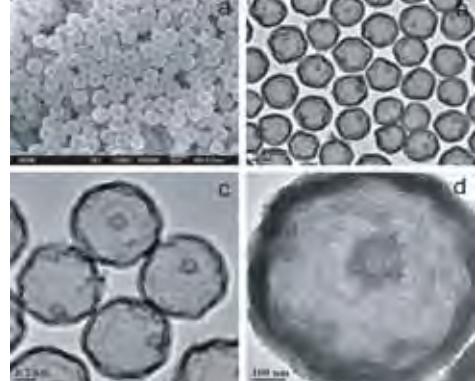
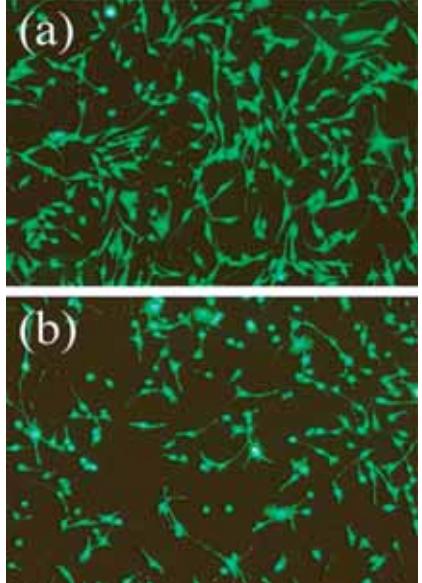


Fig. 1. Dark current and photocurrent under 220-nm light illumination as a function of applied voltage

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<b>Presentation Title:</b> An Efficient Route to Rattle-type $\text{Fe}_3\text{O}_4@\text{SiO}_2$ Hollow Mesoporous Spheres Using Colloidal Carbon Spheres Templates	
<b>Abstract:</b> <p>In the last few years, more and more reports on mesoporous silica based drug delivery systems have been produced<sup>[1]</sup>, because amorphous mesoporous silica materials are a kind of satisfactory drug carrier with the non-toxic nature, adjustable pore diameter, and very high specific surface area with abundant Si-OH bonds on the pore surface. The studies showed that the mesoporous silica spheres with hollow core/mesoporous shell provide much higher drug loading capacity than the conventional mesoporous silica such as MCM-41 and SBA-15, and they also have the sustained release property<sup>[2]</sup>. Furthermore, microspheres are widely accepted as useful drug delivery systems because they can be ingested or injected and present a homogeneous morphology. On the other hand, the superparamagnetic properties of the magnetic nanoparticles (such as <math>\text{Fe}_3\text{O}_4</math>, <math>\gamma\text{-Fe}_2\text{O}_3</math>, and FePt) are of great interest for drug delivery<sup>[3]</sup>. They can carry the drugs and be guided to the targeted organs or locations inside the body, which will facilitate the therapeutic efficiency and avoid the damage of normal organs or tissues due to the drug toxicity before targeting the desired positions.</p> <p>Obviously, to combine the magnetic nanoparticles and hollow mesoporous silica spheres to form rattle-type magnetic core/mesoporous shell silica spheres will realize high drug loading and the magnetic targeting delivery. Here we reported an efficient route to prepare rattle-type <math>\text{Fe}_3\text{O}_4@\text{SiO}_2</math> hollow mesoporous spheres with the large cavities by using colloidal carbon spheres as the templates.</p>	
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<b>Home Page:</b> <a href="http://www.nims.go.jp/icysimat/researchers.html">http://www.nims.go.jp/icysimat/researchers.html</a>	
<b>Presentation Title:</b> ZnO nanostructures-mediated cell viability	
<b>Abstract:</b> <p>The chemical design and synthesis of nanomaterials have fueled the growth of nanotechnology. The unusual physicochemical properties of nanomaterials are attributable to their small size (surface area and size distribution), chemical composition (purity, crystallinity, electronic properties, etc.), surface structure (surface reactivity, surface groups, inorganic or organic coatings, etc.), solubility, shape, and aggregation. Distinct optical, electronic, or magnetic properties can be tuned during chemical synthesis. Currently, more than 350 nanoproducts are already on the market, used in sporting goods, tires, stain-resistant clothing, sunscreens, cosmetics, and electronics and will also be increasingly utilized in medicine for purposes of diagnosis, imaging, and drug delivery. The increased presence of nanomaterials in commercial products raises concerns about adverse effects on the toxicological and environmental effects of direct and indirect exposure to these materials.</p>	
<p>In this presentation, we evaluate the cell viability of different sized and shaped ZnO nanomaterials because of the importance and availability of a rich genre of ZnO nanostructures. The finding of this study will have implication in the chemical design and synthesis of safe nanomaterials for variously applications.</p>	<p>Figure 1 NIH3T3 cell viability after incubated with ZnO nanoparticles (~60 nm) with dose of (a) 0 and (b) 12.5 <math>\mu</math>g/ml for 48 h.</p>
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<b>References:</b>	
<ul style="list-style-type: none"><li>[1] A.D. Maynard, <i>Nature</i> 444, 267 (2006).</li><li>[2] A. Nel, et al., <i>Science</i> 311, 622 (2006).</li><li>[3] N. Lewinski, et al., <i>Small</i> 4, 26 (2008).</li><li>[4] C. A. Poland, et al., <i>Nature Nanotechnol.</i> 3, 423 (2008).</li><li>[5] A. Takagi, et al., <i>J. Toxicol. Sci.</i> 33, 105 (2008).</li><li>[6] Z. L. Wang, <i>Materials Today</i> 7, 26 (2004).</li></ul>	

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<b>Presentation Title:</b> Ruthenium complexes for artificial endonucleases: DFT analysis of ligands and potential binding interactions with DNA	
<b>Abstract:</b> <p>Restriction endonucleases are enzymes that are able to cut DNA in a reparable way at well-defined sequences. As such, they are important tools in genetic and metabolic engineering. Unfortunately, naturally-occurring enzymes recognize a limited range of sequences and it is almost impossible to customize them. A possible alternative to protein-based endonucleases is to use ruthenium complexes, some of which are known to cleave DNA in the presence of light, usually by oxidation of a nucleobase. Sequence specificity can potentially be achieved by tethering short oligonucleotides to the metallic complex. However, these organometallic systems are not free of problems. One of them is that the oxidative pathway which the reaction follows makes recovery of the original, re-ligated DNA difficult.</p> <p>A new kind of complex has been found (see Fig. 1), which is able to cut DNA following a hydrolytic pathway, similar to that of natural enzymes [1]. This is a very promising system. However, the details of the mechanism are not understood. In particular, hydrogen-bonding seems to be important, but the structure of the network is not known. In addition, ligand functionalization is key to reactivity. We use DFT, as implemented in our linear-scaling code Conquest [2], to gain insight into the reaction. As a first step, this contribution presents electron-density calculations of elementary Ru-complex ligands, notably bipyridines (bpy) substituted by electron-donating and electron-withdrawing groups, as well as glycouril. Population analysis of the densities, along with preliminary docking of the glycouril complex into B-DNA, aimed at identifying binding sites, will also be discussed.</p>	
<b>References:</b> <ul style="list-style-type: none"> <li>[1] M.S. Deshpande, A.A. Kumbhar and A.S. Kumbhar <i>Inorg. Chem.</i> (2007) <b>46</b>, 5450-5452</li> <li>[2] D. Bowler, R. Choudhury, M. Gillan and T. Miyazaki <i>Phys. Stat. Sol. B</i> (2006) <b>243</b>, 989-1000</li> </ul>	

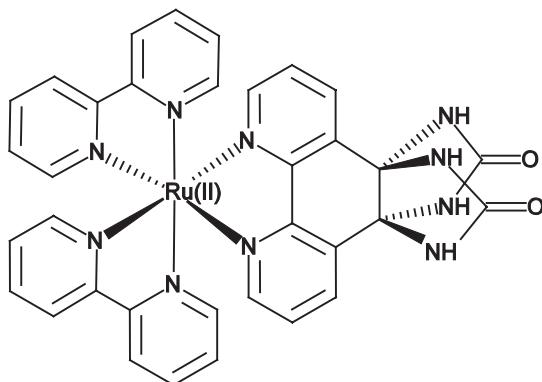
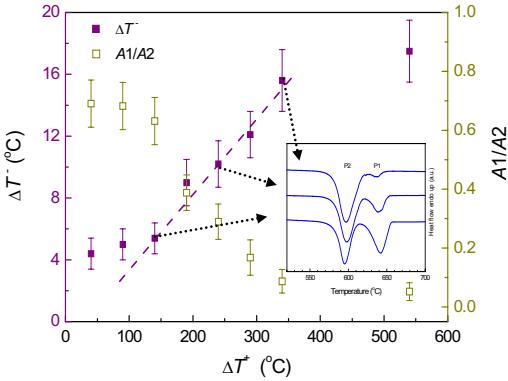


Fig. 1: Ruthenium bisbpy,bpyglycouril: a complex able to hydrolyze DNA

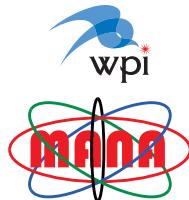
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<b>Presentation Title:</b> Effect of liquid superheating on liquid supercooling of Al particles	
<b>Abstract:</b> The freezing process of liquids is known to be prone to the influence of catalysts. Despite the significance for industry applications, it is still not clear how various extraneous particles (e.g. grain refiners or impurities) work to catalyze the freezing of liquids. <sup>1</sup> The liquid superheating (thermal history) has been found to have a significant effect on the supercooling behavior of various metals and alloys, which is believed to be related to the catalyzing effect of extraneous particles. <sup>2,3</sup> It is believed that the key to understand the catalyzing effect of extraneous particles on freezing of liquids and the $\Delta T^-$ - $\Delta T^+$ relationship lies in the characteristics of the solid/liquid interfacial structure. <sup>1</sup>	 <p>Figure 1 is a plot showing the variation of supercooling (<math>\Delta T^-</math>) and relative peak area (<math>A_1/A_2</math>) as a function of liquid superheating (<math>\Delta T^+</math>). The main plot has two y-axes: the left y-axis represents <math>\Delta T^-</math> in °C (0 to 20), and the right y-axis represents <math>A_1/A_2</math> (0.0 to 1.0). The x-axis represents <math>\Delta T^+</math> in °C (0 to 600). Data points for <math>\Delta T^-</math> (purple squares with error bars) and <math>A_1/A_2</math> (yellow squares with error bars) are plotted. A dotted line connects the data points. An inset shows DSC curves for P1 and P2 at different <math>\Delta T^+</math> values, with the x-axis labeled 'Temperature (°C)' and the y-axis labeled 'Relative end ΔH (ΔH₀)'.</p>
	<b>Fig.1</b> Variation of $\Delta T^-$ for P1 and relative peak area ( $A_1/A_2$ ) as a function of $\Delta T^+$ in Al small particle sample. Insert shows the freezing DSC curves for different $\Delta T^+$ as indicated.
	In the present study, the effect of melt superheating ( $\Delta T^+$ ) on supercooling ( $\Delta T^-$ ) of Al particles were studied by using differential scanning calorimeter (DSC). As shown in Fig.1, in which $\Delta T^-$ is taken as the difference between the onset temperature of P1 and $T_0$ of Al, and $\Delta T^+$ is taken as that between the liquid temperature and $T_0$ of Al, an approximate linear $\Delta T^+$ dependence of $\Delta T^-$ was obtained in the $\Delta T^+$ range of 140-340 °C, which was found to be related to the catalyzing effect of impurity particles. A core-shell model was further proposed to interpret the linear $\Delta T^-$ - $\Delta T^+$ relationship successfully, with the supposing that a transitional region (shell) exists between the impurity particle (core) and the host liquid (Al). The study provided information on the catalyzing mechanism of impurity particles and characteristics of the solid/liquid interfacial structure. The model also rationalized the sluggishness of melting process of high-melting particles in liquids.
<b>References:</b>	<p>[1] A. L. Greer, Nat. Mater. <b>5</b>, 13(2006).  [2] D. Turnbull, J. Chem. Phys. <b>18</b>, 198 (1950).  [3] W. Luzny, J. Phys.: Condens. Matter <b>2</b>, 10183 (1990).</p>

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<b>Presentation Title:</b> Facile Synthesis of Ultralong Cadmium Chalcogenide Nanotubes by Sacrificial Template Route from 1D Cadmium Hydroxide Nanowires Bundles	
<b>Abstract:</b> <p>During the past decade, with a pioneer discovery of WS<sub>2</sub> nanotubes (NT), various kinds inorganic NT have been prepared owing to their unique physical and chemical properties and potential applications in nanoscale devices with diverse functions. The NT of inorganic semiconductors can be considered a new class of materials which exhibit properties quite different from those of their bulk form as the physical properties and electronic structure combine characteristics of both two dimensional (2D) and one dimensional (1D) materials. Among the many approaches to form the nanotubes, sacrificial template route more efficient and advantageous route to form size tunable nanotubes.</p> <p>Herein, we report a cost effective fabrication method of NT directly onto the substrate over physically a large area using sacrificial template of 1D structures grown by a simple soft chemical method, low temperature approach. As an example, a sacrificial template approach for synthesis of ultralong CdX NT with high aspect ratio, composed of nanoparticles from a template of Cd(OH)<sub>2</sub> nanowires bundles (NB) is described here. The present work demonstrated an effective method for the synthesis of ultralong CdX NT via reaction with X<sup>2-</sup> ion source employing Cd(OH)<sub>2</sub> NBs as the sacrificial template. A simple anion exchange route was designed to synthesize CdX NT using the Cd(OH)<sub>2</sub> NB precursor nanowires as both the Cd source and the template. In the first step, synthesis of ultralong Cd(OH)<sub>2</sub> NB onto substrates was carried out via a soft solution chemistry as described in ref.[1] When the Cd(OH)<sub>2</sub> NB coated onto the substrates were reacted with an aqueous solution of X<sup>2-</sup> the anion exchange reaction takes place and due to the lower solubility of CdX in the solution nanocrystals are formed onto the surface of the precursor NBs. Further the diameter tunability of the NT is possible via precursor NB diameter.</p>	
<b>References:</b> [1] V. R. Shinde, H. S. Shim, T. P. Gujar, H. J. Kim, W. B. Kim <i>Adv.Mater.</i> <b>2008</b> , <i>20</i> , 1008-1012.	





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