MANA Progress Report

Research Digest 2008

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

National Institute for Materials Science (NIMS)

Preface

Masakazu Aono
MANA Director-General

The International Center for Materials Nanoarchitectonics (MANA) was one of five institutions selected for the Ministry of Education, Culture, Sports, Science and Technology (MEXT)-sponsored World Premier International (WPI) Research Center Initiative. It was launched in October 2007 under the direction of the National Institute for Materials Science (NIMS). The project concept for MANA aims to build a highly visible, world-class nanotechnology materials research center that attracts top researchers from around the world and that the world's best researchers want to visit and be a part of. To achieve this, MANA promotes challenging, cutting-edge fundamental nanotechnology research by utilizing the skills of its multinational, independent researchers. It contributes to the creation of innovation and the development of science and technology through the invention and discovery of new materials and devices. MANA research is grouped into the four research fields: Nano-Materials, Nano-System, Nano-Green and Nano-Bio.

The part Research Digest of the MANA Progress Report 2008 summarizes the research activities of *MANA Principal Investigators*, *MANA Independent Scientists* and *ICYS-MANA Researchers* for the time from the Inauguration of MANA in October 2007 until December 2008. A *MANA Principal Investigator* is an internationally known world-top class scientist, who takes the main role to achieve the MANA research targets and serves as a mentor for younger scientists. A *MANA Independent Scientist* is a younger researcher at NIMS, who works full-time for MANA and can perform his own research independently. *ICYS-MANA Researcher* is a position for postdoctoral fellows selected from all over the world by open recruitment. ICYS-MANA Researchers perform their own research independently by receiving advice from Mentors and MANA Principal Investigators. Information about the MANA research achievements (e.g., list of publications, list of patents) is given in the MANA Progress Report 2008.

We look forward to your continued understanding and support of MANA activities.

MANA Research Digest 2008

MANA Principal Investigators

Nano-Materials Field

Nano-System Field

Nano-Green Field

Nano-Bio Field

MANA Independent Scientists

ICYS-MANA Researchers

Inorganic Nanosheets

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1. Outline of Research

We aim at developing a new nanofabrication process involving organization of our original nanomaterials, inorganic nanosheets, through wet-processes, which allows architectural design of materials from a level of crystalline lattice planes. New innovative materials will be created by utilizing advantages of the wet-process nanofabrication approach.

We will develop a wet-process approach for organizing the functional nanosheets into multilayer or superlattice assemblies with a finely controlled nanostructure. Based on the exotic approach with nanosheets, we will establish the high designing ability and controllability over nanostructures with a precision down to 1 nm, which is comparable to that of advanced vapor-phase deposition techniques.

In the second stage, we will take challenges to tailor exotic nanostructured materials comparable to artificial lattice systems through nanoscale assembly of nanosheets and a range of foreign species, based on the new nanofabrication process. We plan to create novel nanostructured materials or nanodevices with a sophisticated function. Followings are some of selected targets.

(1) High-*k* nanofilms, which work at a thickness down to several nanometers.
(2) Transparent magnetic films, which act in response to UV or short-wavelength visible light.
(3) A new technique, which promotes the growth of high-quality films of functional crystals.

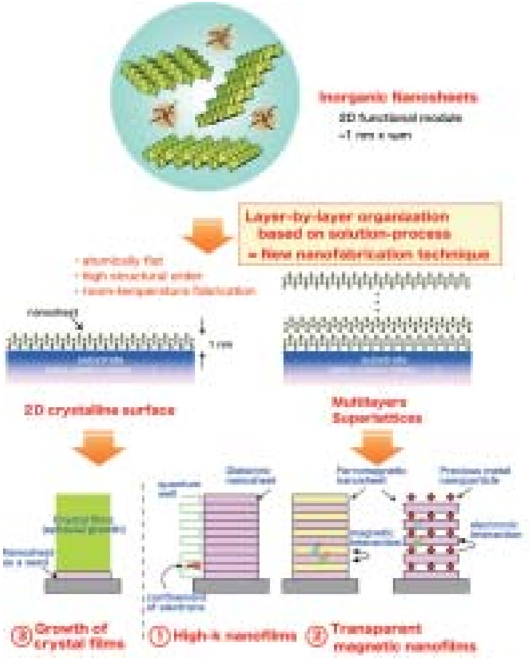

Fig. 1. Conceptual explanation of the research plan.

2. Research Activities

(1) Synthesis of New Functional Nanosheets

We have successfully synthesized new oxide nanosheets such as $Eu_{0.56}Ta_2O_7$[1] (Fig. 2), $(K_{1.5}Eu_{0.5})Nb_3O_{10}$ and $Cs_4W_{11}O_{36}$ by soft-chemical delamination of precursory layered compounds. The former two show photoluminescence and the latter exhibits photochromic properties, contributing to expansion of functional nanosheet library.

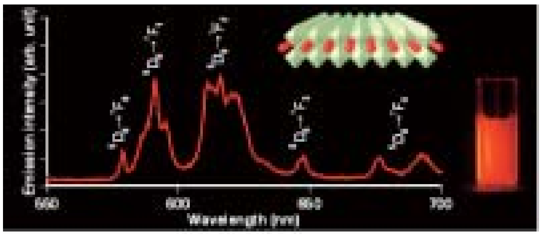

Fig. 2. Emission spectrum of $Eu_{0.56}Ta_2O_7$ nanosheet. Red emission is visible by naked eye as shown in inset.

(2) Synthesis of a New Layered Rare-Earth Hydroxides

We found that a new class of layered hydroxides can be prepared via homogeneous precipitation of rare-earth salts.[2] Rietveld analysis on SR-XRD data revealed a unique layered structure of the compounds having a stoichiometry of $Ln_2(OH)_5Cl \cdot nH_2O$ (Fig. 3). The compounds are very attractive because of their promising features of anion-exchange reactivity, optical and magnetic properties.

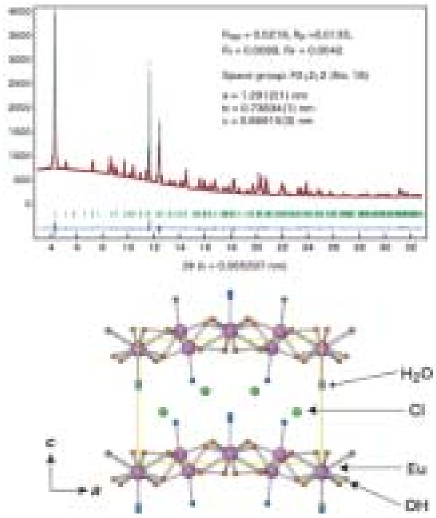

Fig. 3. Rietveld refinement pattern and crystal structure for $Eu_2(OH)_5Cl \cdot nH_2O$.

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Dynamic Functions of Supramolecular Materials in Hierarchic Construction

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1. Outline of Research

In our group, design, synthesis, and fabrication of organic materials and organic/inorganic hybrids with nano-sized structural features have been done based on bottom-up supramolecular approaches from unit molecular structures, leading to novel supramolecular materials in nano, micro, and bulk dimensions.[1] Construction of nano-sized structures was demonstrated through formation of two-dimensional arrays of organic molecules and inorganic substances.[2-4] Various microscopic morphologies were successfully constructed through self-assembled process.[5-7] Structure transcription of molecular assembly resulted in well-structured bulk materials.[8, 9] In addition to material fabrication, novel functions such dynamic molecular machine,[10] chemical non-volatile memory,[11] and nanorod-driven display control[12] have been developed. Especially, hierarchic structural design of supramolecular materials has successfully resulted in world-level innovation such as auto-modulated drug delivery system[13] and highly cooperative sensor[14] as shown below.

2. Research Activities

(1) Auto-Modulated Drug Delivery System Using Mesoporous Nanocompartment Film[13]

Mesoporous nano-compartment films composed of silica particles, hollow silica capsules, and polyelectrolytes (Fig. 1) have been fabricated through the layer-by-layer assembly. The resulting films showed unusual auto-modulated stepwise release of entrapped water molecules. This phenomenon is originated from the non-equilibrated rates between evaporation of water from the mesopore channels to the exterior and the capillary penetration of water from container interior to the mesopore channels. It was generalized as *stimuli-free* auto-modulated release of other drug substance such as fragrances. These films are promising materials for drug delivery, likely leading to improvements in therapeutic efficacy, while encapsulation and release of different drugs may expand the possible applications of this system in a variety of biomedical fields.

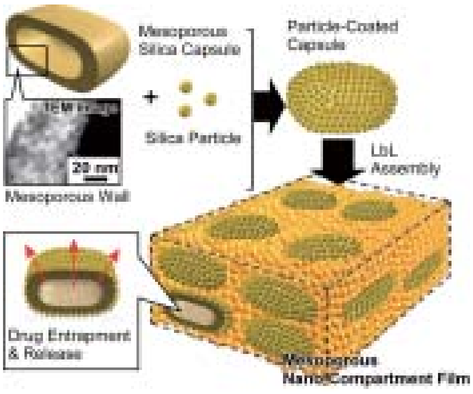

Fig. 1. Schematic illustration of silica particle/capsule nanocompartment film.

(2) Highly Cooperative Sensor Using Mesoporous Carbon Films[14]

We have made the initial demonstration of layer-by-layer assembly of mesoporous carbon materials onto a quartz crystal microbalance plate, and subsequently used it for sensing of nonionic aqueous guests (tea components), caffeine, catechin, and tannic acid (Fig. 2). High selectivity for tannic acid over the others was obtained. Since the system used provides a very simple in situ measurement for material adsorption into size-controlled nanospaces, the highly cooperative adsorption of neutral molecules within size-defined carbon nanospaces in the liquid phase was serendipitously discovered.

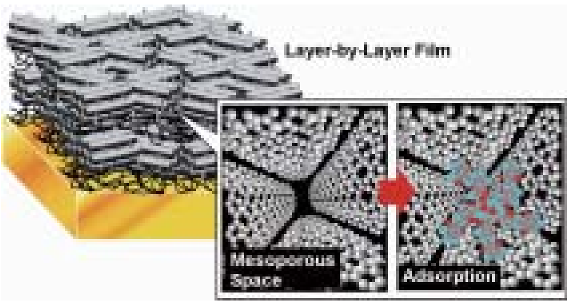

Fig. 2. Schematic illustration of layer-by-layer films for mesoporous carbon sensor.

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Novel Inorganic Nanotubes and Nanowires

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1. Outline of Research

Our ultimate goal is creating novel inorganic nanotubes and nanowires; exploring their applications, including their optoelectronic applications, composites materials fabrication etc.

One dimensional nanomaterials we are currently interested in nitrides and sulfides, such as AlN, BN, GaN and ZnS, CdS nanostructures etc. We expect one-dimensional morphologies like nanotubes and nanowires could enrich their applications. For example, these nanostructures possess semiconducting wide band gaps ranging from 2-6 eV, which may enable us to fabricate various optoelectronic devices such as photodectors, photoemitters etc. The prefect one dimensional crystal may result in better quantum efficiency and easy fabrication of devices. In addition, some of the nanostructures chosen have special properties except being a semiconductor. For example, the super high thermal conductivity (BN, AlN), great mechanical strength (BN) etc. These properties make them be novel nanofillers for composites materials.

Based on the ultimate goal and our current researches, we set up following three sub-themes. They can be effectively coordinated. (Fig.1)

(i) Developing highly effective synthesis method for various semiconductor nanomaterials;
(ii) Developing highly thermo-conductive electrically insulating polymeric composites based on novel nanofillers developed;
(iii) Functionalization of nanostructures to extend their various applications.

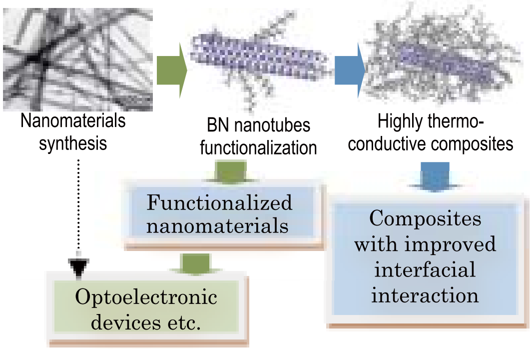

Fig. 1. Three sub-themes and their organic coordination.

2. Research Activities

1. Highly thermo-conductive electrically insulating polymeric composites.[1]

A novel filtering-absorbing method was developed to embed high concentration BNNTs in various polymers. More than 20-fold thermal conductivity improvement in BNNT-containing polymers was obtained. (Fig.1) The coefficient of thermal expansion (CTE) of BNNT loaded polymers was dramatically reduced due to interactions. This 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.

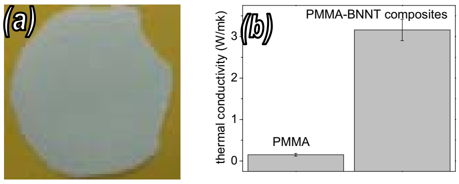

Fig.1. (a) Image of a mat of PMMA-BNNTs composites; (b) improvement of thermal conductivity of PMMA-BNNT composites.

2. Aqueous noncovalent functionalization and controlled near-surface carbon doping of BNNTs.[2]

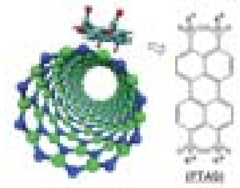

Fig. 2. Schematic of PTAS functionalization of BNNTs.

Noncovalent functionalization of BNNTs in the aqueous solution, through which the carboxylate modified BNNTs have been prepared for the first time. Moreover, an innovative methodology for the controlled near-surface C-doping of BNNTs was realized. As a result of doping, novel B-C-N/BN coaxial nanotubes have been fabricated on a large scale, and their *p*-type semiconducting behaviors were elucidated through gate-dependent transport measurements.

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In-situ TEM Property Analysis of Nanotubes

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1. Outline of Research

Our ultimate goal is to understand the nanotube (and related structures: nanowires, nanobelts, nanosheets) electrical and mechanical properties, in particular, on the individual structure level, using STM and AFM holders integrated within a high-resolution transmission electron microscope (HRTEM), and to manipulate and engineer the nanostructures toward their smart applications in diverse nanotechnologies.

This top-notch research allows one to simultaneously use a TEM instrument as the nanomanipulator ("the hand"), and as the dedicated high-spatial resolution (better than 1.7Å) analyzer ("the eye"). The systems of our interest include various inorganic nanotubes made of C, BN, CN, BCN, ZnS, ZnO, CdS, GaN etc. These may additionally contain metal and ceramic fillings. Under two-terminal electrical probing within TEM (STM-TEM), Fig. 1a, numerous new and interesting nanoscale phenomena are supposed to be uncovered, namely, rectifying transport behavior, deformation-induced electrical transport, piezoelectrical response, Joule-heating-induced nanostructure and/or its filling melting, sublimation, interdiffusion and recrystallization. And during mechanical testing (AFM-TEM), Fig. 1b, individual nanostructure Young modulus, yield stresses, brittle and plastic failures, superplasticity (never been verified to date) are envisaged to be fully understood. This should lead to smart integration of the nanotubes/nanowires into novel nanoscale composites and heterostructured systems.

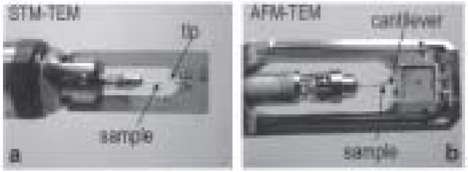

Fig. 1. Experimental setups within the STM-TEM (a) and AFM-TEM (b) holders. The locations of nanotube samples, gold STM tip and Si cantilever are marked.

2. Research Activities

(1) Electrical transport in N-doped CNT [1,2]

Deformation studies of individual nanotubes together with experiments on their complex cross-junctions showed that the nanotube *I-V* characteristics are dominated by the contact area established between the tube and gold electrodes. A surprising observation was the capability of the CN_x nanotubes to remain purely metallic even under significant stress and with highly defective structures. Current-induced failure showed that the regions with diameter variations, which are assumed to be defect-rich, were responsible for the structure rupture.

(2) Nanopipettes made of halide-filled C nanotubes[3,4]

Encapsulated nanograins of CuI have been sequentially discharged from individual C nanotubes. It was possible to manipulate the filling contents at levels better than femtograms (10^{-18} g). Changes in electrical resistance and filling ratios were followed *in-tandem*, in real-time. It was shown that the pulsed-release of the halide was directly related to the overall conductance of the nanotubes.

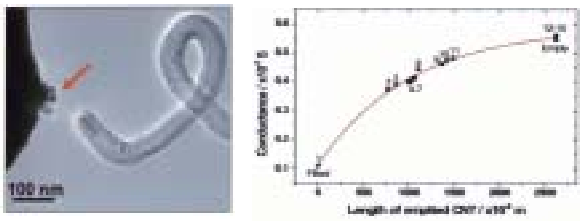

Fig. 2. (left) CNT pippette in action: a view of the NT-gold contact region displaying Cu nanocrystals (arrowed) deposited in steps from a CuI-filled nanotube under passing sequential electrical pulses; (right) overall CNT conductance vs the emptied nanotube length.

(3) Effect of crystalline filling on the mechanical response of C nanotubes[5]

The electrical and mechanical properties of the same hybrid C nanotube before and after removal of the core Ga-doped ZnS semiconductor have been analyzed using the conducting AFM-TEM setup. For the first time we directly observed that the encapsulated material substantially changes the mechanical response of the C tubular container. Since the extent of filling is operator-controlled, this provides a new technological way to tune the stiffness of hybrid tubes and nanocomposites.

Fig. 3. (a) C tube filled with Zn(Ga)S. The current (e-) causes Joule heating which leads to the core discharge; (b) tube seen in (a) after partial removal of its core. (c) Plastic deformation of the emptied, and thus weakened structure fragment, under compression in TEM.

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Nanostructured Metallic Materials

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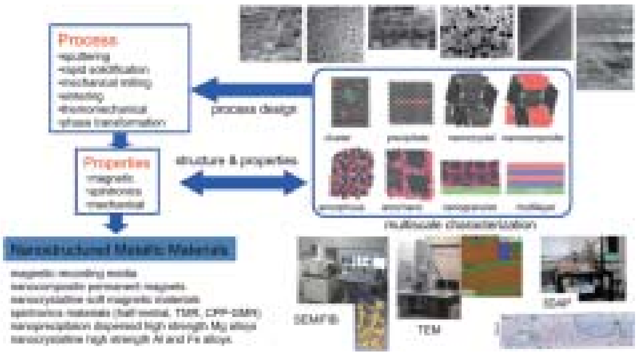
1. Outline of Research

The purpose of this study is to obtain better understandings of structure-property relationships of various nanostructured metallic materials to develop the materials with superior properties for energy saving and data storage. The specific subjects for this study are: 1) nanostructure investigations of Mg and Al alloys for developing high strength light alloys for weight reductions of transportation vehicles, 2) nanostructure and nanochemistry of the grain boundaries of Nd-Fe-B magnets for developing higher coercivity magnets, 3) interfacial nanostructure control of spintronics devices for achieving better magnetotransport properties.

Understanding the structure-property relationships of the above materials are essential to design and develop the materials with superior performances. However, because of their extremely fine size, characterizations of the structure and chemistry have been challenges. In this work, we carry out multiscale characterization of structural, magnetic, and spintronics materials by using high resolution scanning/transmission electron microscopy and atom probe tomography. The micro/nanostructures characterized by these techniques are compared with the property changes to establish the structure-property relationships of the above materials. This information will be used to design/process the nanostructured materials with superior mechanical, magnetic and transport properties.



2. Research Activities

To develop ultrahigh density recording media for the areal density of higher than 1 Tbit/in^2, we successfully fabricated L1$_0$ FePt–C nanogranular perpendicular anisotropy films with narrow size distribution on oxidized Si substrates with (100) textured MgO intermediate layer as shown in Fig. 1. A small amount of C (<12%) addition in FePt (4 nm) film by cosputtering results in the formation of interconnected FePt particles, while higher C addition led to the formation of well-isolated L1$_0$ FePt nanoparticles with a strong c-axis texture. The FePt particle size could be reduced to 5.5 nm with narrow size distribution by fine-tuning the FePt thickness. Perpendicular coercivity of the FePt–C films is controllable between 8 and 15 kOe with high squareness. These results demonstrate that the FePt-C system can accomplish the nanogranular structure suitable for ultrahigh density perpendicular recording media. Fig. 1

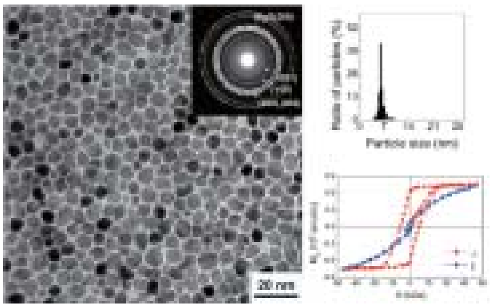


Fig. 2. L1$_0$-FePt-C perpendicular magnetic granular thin film.

To develop ultrafine grained high coercivity anisotropic permanent magnets, we have investigated the microstructure change of hydrogenation disproportionation desorption recombination (HDDR) processed Nd$_{12.5}$Fe$_{73}$Co$_8$B$_{6.5}$ powders during the desorption recombination (DR) stage to understand the mechanism of the coercivity development in the DR process. A uniform Nd-enriched layer was found to form along the grain boundaries when coercivity starts to increase in the DR process, which should be the main reason for the coercivity development. However, the composition of this grain boundary layer was found to contain a high concentration of ferromagnetic elements.

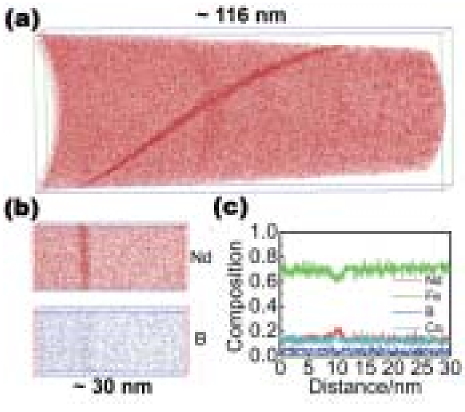


Fig. 3. 3DAP analysis of grain boundary in Nd-Fe-B based nanocrystalline magnet.

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Photo-ferroelectric Materials

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1. Outline of Research

We set up NIMS Overseas Operation Office at University of Washington to promote collaborative research programs between NIMS and UW in interdisciplinary research fields, such as medical science, materials engineering, mechanical engineering, and aero-space science. In this project, four research sub-themes were set as follows.

1) *"Tunable IR Wavelength Conversion Materials and Devices for Dental Applications":*

This project is to develop a new capability with potentially wide application of tunable IR wavelength conversion devices using a quasi-phase-matched optical parametric (QPM) generation. Anticipated outcome of this project is to develop a simple, compact, robust and maintenance free module for tunable IR wavelength conversion for biological, atmospheric, and materials research. In this research, EMSL/PNNL plays a role in developing and testing proposed tunable IR wavelength conversion modules in collaboration with NIMS, who originally demonstrated QPM using single crystal materials of Mg doped SLT that were developed in NIMS. Development for a clinical laser is lead by UW-Dentistry. UW-MSE assesses the damage created by laser and nano-structural characterization for further improvement of the materials systems.

2) *"Charged Molecules Manipulation on Nano-Domain Patterned Ferroelectric Templates":*

In this research, multi-functional properties of ferroelectric lithium niobate (LN) and lithium tantalate (LT) single crystals, such as piezoelectric, pyroelectric and photo-voltaic effects, are used to control surface potentials and charges of the materials through external fields. Nanoscale domain patterning, a technique also developed in NIMS, is employed to pattern the surface properties. In the vicinity of surfaces, polarization charge by pyroelectricity and carrier supply by photovoltaic effect result in domain specific adsorption of charged ions, molecules (including designed DNA) and nano-particles from the environment. We aim to create novel functional template using the surface potential controlled ferroelectric crystals. This program is performed under the collaboration with Department of Chemistry and Mechanical Engineering of UW.

3) *"Polymer Blends for Nano-structured Photovoltaic Devices":*

This research focuses on the physical chemistry of nanostructured materials with potential applications for low cost photovoltaic devices (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_{61}-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.

4) *"Nano-Wire Based Thermoeletric Devices Using Nano-cage Structure Materials.":*

This program is focusing on the direct patterning of electrically conductive nano-wires in the material of low thermal conductivity such as nano-cage structure materials. ELB technique is used to draw conductive pass ways on the surface of material, for example, "mayenite" which exhibits nano-cage structure. NIMS explores and grows materials and UW investigates thermo-electric properties of nano-wires fabricated on the surface aiming at a new type of thermo-electric device.

2. Research Activities

1) Ferroelectric domain patterning by polarization inversion was performed by a tip-biased lithography using a contact voltage mode. This technology enables nano-scaled rewriteable domain patterning with a comparative high speed.

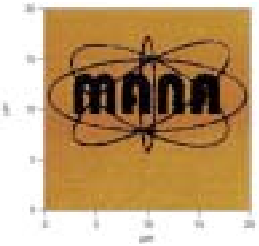

Fig.1. PFM image of domain pattern: the dark parts are inverted domains having +Z face surface.

2) We created 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 was 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, Fig.2 and 3 are AFM ac-mode topographic and fluorescent images of P3HT: PCBM films spin-coated on OPA-patterned substrates showing a segregation of P3HT-enriched in dark areas, and PCBM-enriched in bright areas.

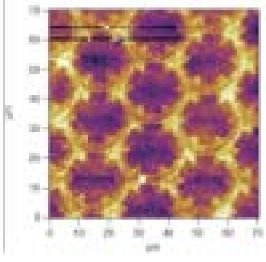

Fig.2. AFM topographic image.

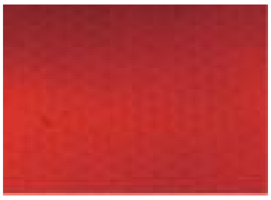

Fig.3. Fluorescent image. Film thickness of ~150 nm, excitation at 535-565 nm, emission at 590 nm.

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Novel Functional Materials

MANA Principal Investigator **Eiji TAKAYAMA-MUROMACHI**
MANA Research Associate Youguo Shi, Yanfeng Guo, Rusakov Dmitriy

1. Outline of Research

We aim to explore new key materials, and new phenomena and functions. We are expecting development of new high Tc superconductors, magnetic materials, ferroelectric materials, multi-ferroic materials, etc. Our target systems are not only oxides but non oxides such as nitride, arsenide, selenide, etc.

In order to accomplish this purpose, we will utilize two unique synthesis techniques and their combination. First technique is high-pressure synthesis. NIMS has a long history of development of high-pressure synthesis technique. Thanks to this, we can use world highest class high-pressure apparatuses. The second technique in materials preparation is soft-chemical synthesis. The soft-chemistry uses chemical reactions at or near room temperature such as intercalation and deintercalation of ions, ion exchange, chemical (or electrochemical) oxidation and reduction, etc. and is sometimes quite promising method to prepare metastable materials. The combination of the two methods, namely control of the pressure field and chemical field is really a powerful way for materials exploration research.

We set following three sub-themes and are conducting the materials exploration research effectively by organically coordinating these sub-themes (Fig. 1).

(i) Materials synthesis utilizing high-pressure and soft-chemical techniques,
(ii) Structure analysis for average and local structures,
(iii) Measurements of various physical properties for newly discovered materials.

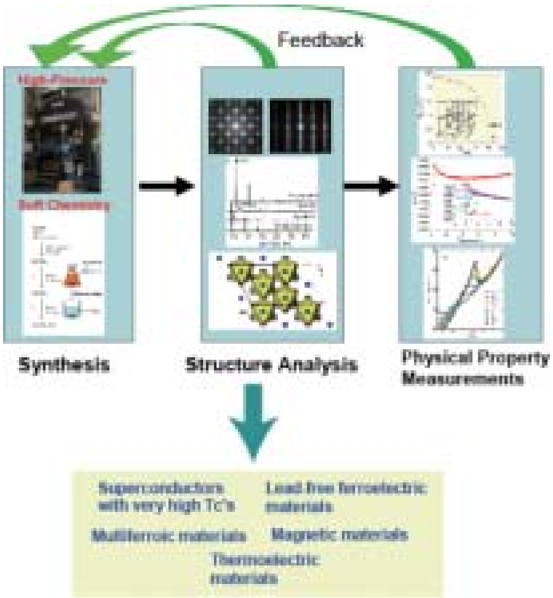

Fig.1. Three sub-themes and their organic coordination for conducting effective materials exploration research.

2. Research Activities

(1) Synthesis and Measurements of Superconducting Properties of the Iron Oxyarsenide $TbFeAsO_{0.85}$[1)]

The iron oxypnictide superconductor reported by a Tokyo Institute of Technology group was an epoch discovery in research of high-*Tc* superconductivity. We synthesized the iron oxyarsenide $TbFeAsO_{0.85}$ by the high-pressure method. A high quality polycrystalline sample was obtained and characterized by measurements of magnetic susceptibility and electrical resistivity. Bulk superconductivity with *Tc* of 42 K was clearly established (Fig. 2).

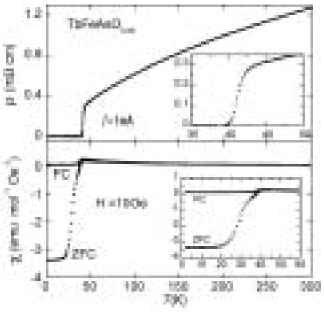

Fig. 2. Electrical resistivity and magnetic susceptibility of the polycrystalline $TbFeAsO_{0.85}$.

(2) Discovery of NaV_2O_4: A Quasi-1D Metallic Antiferromagnet with Half-Metallic Chains[2)]

We have synthesized, grew single crystals and characterized the basic physical properties for a new mixed-valent vanadium oxide, NaV_2O_4 (Fig. 3), which shows remarkable magnetic and electrical properties. First-principles calculations indicate that half-metallic ferromagnetism is found on the chains, whereas the behavior of the magnetization is consistent with antiferromagnetic order, with moments collinear with the chains.

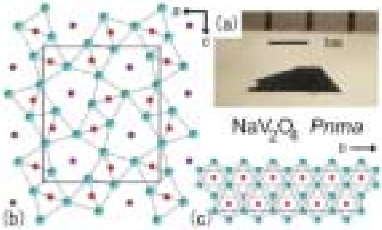

Fig. 3. (a) A single crystal of NaV_2O_4 (1.779 mg). (b) Schematic structural view of NaV_2O_4, drawn from the x-ray result and (c) a local structural view of the double chain.

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Optoelectronic Materials

MANA Principal Investigator **Naoki OHASHI**
MANA Scientist Yutaka Adachi, Isao Sakaguchi
MANA Research Associate Yong-Zhao Yao, Jian-Yong Li, Bao-E Li, Yu-Hua Zhen
Graduate Student Ryota Matsuoka, Kenji Matsumoto

1. Outline of Research

Development of nano-materials and nano-structures are regarded as breakthrough for achievement of highly efficient society with less energy consumption and harmful wastes and with new earth friendly energy source. Consequently, there are many needs in the field of optoelectronic materials, such as high efficiency of light emission, high efficiency of signal processing and so on. Thus, we decided to devote ourselves for investigate materials and structures for optical and electronic applications in order to achieve sustainable development of human society. In particular, we aim to develop oxide materials for optical and electronic applications, because oxides exhibit many useful functions, such as ferroelectricity, piezoelectricity, and luminescence. To this purpose, we believe that the fundamental knowledge on oxide is still crucial. For example, so-called size effect is one of the most important issues in the filed of oxides, but the quantitative understanding of such size effect is under development. Thus, we start from the understanding of fundamental but unsolved problems in oxide. Thus, we set following two sub-themes to be investigated.

(i) Properties of oxide interface and surface.
(ii) Self-organization behavior in oxide system.

2. Research Activities

(1) Electronic structure of metal oxide[1-3]

In order to understand chemical and physical activities of oxide surface, we started to utilize hard x-ray photoelectron spectroscopy to investigation of the electronic structure in oxide. We studied band lineup in (Zn,Mg)O pseudo-binary alloy system, and revealed that the Fermi level in this alloy compounds were situated close to the bottom of conduction band. As this alloy system is of crucial importance for fabrication of oxide electronic devices this knowledge gives important knowledge on designing the devices structures, such as (Zn,Mg)O/ZnO HEMT structures.

(2) Interfacial structure at oxide/oxide interface[4,5]

Electronic structure at oxide/oxide interface has been studied in terms of polarity relationship. Many oxide semiconductors have polarity in their crystal structures. For example, wurtzite-type crystals has anion terminated (000-1) face and cation terminated (0001) face. Such polarity has to be considered on fabrication of heterostructure devices, because those polarization affects to the carrier conferment and charge separation at heterostructure interface. We illustrated the effect of the crystalline polarization relationship at ZnO/insulator/ZnO interfaces to their electronic properties[4] and the effect of dopants on determination of the polarity of ZnO film crystals hetero-epitaxially grown on sapphire substrate.[5] As can be seen in Fig. 2, ZnO films having (0001) face could be obtained when Al-doped ZnO was grown on sapphire substrate and, in contrast, those having (000-1) face could could be obtained when the umdoped ZnO was grown on sapphire.

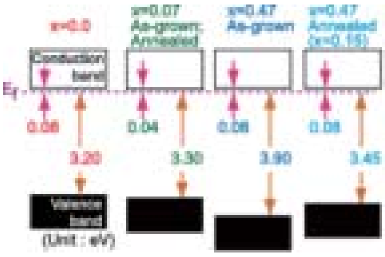

Fig. 1. band lineup in $(Zn_{1-x}Mg_x)O$ system referring to Fermi level.

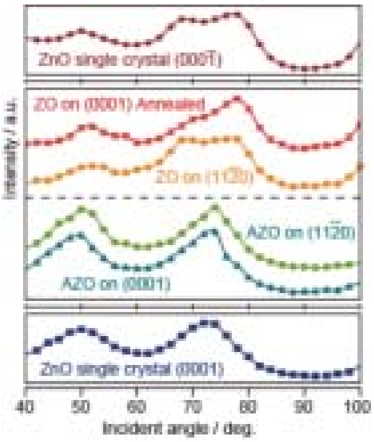

Fig.2. CAISSIS spectra of ZnO, indicating pure ZnO (ZO) and Al-doped ZnO (AZO) films on sapphire substrate have (000-1) and (0001) face, respectively.

(3) Chemical diffusion in oxide in terms of Fermi level effect[6]

The thermal relaxation behavior of ion implanted ZnO was investigated to obtain knowledge necessary for fabrication of ZnO based devices. In this way, we revealed that diffusion of the implanted group III elements is governed by so-called Fermi level effect and could not be understood by simple Fick's model just assuming gradient of the elemental distribution. We demonstrated that the diffusion profile of implanted group III elements in ZnO was favorable for fabrication of heavily electron doped source and drain in ZnO based thin film transistor structures, and this may be an elemental phenomena involved in the self-organization processes.

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Structure Controlled Ceramics

MANA Principal Investigator **Yoshio SAKKA**
MANA Research Associate Chunfen Hu
Graduate Student Gustavo Suarez, Salvatore Grasso, Mamiko Kawakita

1. Outline of Research

We plan to fabricate highly structure controlled ceramics that show novel properties through the development of nanoparticle processing. Especially the broad objective of the research is to develop novel colloidal processing techniques for preparation of advanced ceramic materials. One is for deposition of 2-D and 3-D patterned/ ordered array of functional inorganic nanoparticles.

An important aspect of the study will consist of novel colloidal processing by external srimulation such as strong magnetic field, electric current, etc. to obtain textured/laminated ceramics to be able to tune and enhance the desired functional properties. Recently pulsed electrophoretic deposition (EPD) have been demonstrated to produce bubble-free deposits from aqueous suspension. Also the alignment of feeble magnetic ceramics by EPD in a strong magnetic field is developed at NIMS. Both techniques are expected to be a powerful method to produce highly structure controlled ceramics resulting in excellent functional ceramics.

Another important aspect will consist of novel sintering techniques such as miliwave sintering and spark plasma sintering (SPS). Both are relatively new materials processing technologies and extremly short heat processing time and are expected to be powerful methods for obtaining nanostructure materials. The temperature measurement of the sample during sintering is the most severe limiting factor. Computer modeling is generally considered an effective means to solve above problems provided that the models are designed to capture the essential multiphysics of actual SPS apparatus and are reliably tested against experiments. This self-consistent experimental/numerical methodology is expected to develop a novel sintering techniques.

We set following three sub-themes and are conducting the materials exploration research effectively (Fig. 1).

(i) Tailor-made nanoparticle preparation,
(ii) Fabrication and application of textured and laminate ceramics,
(iii) Development of novel sintering technology.

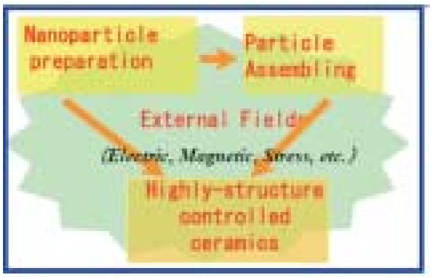

Fig.1. Three sub-themes and their organic coordination for conducting effective materials exploration research.

2. Research Activities

(1) Formation of crystalline-oriented titania thin films by electrophoretic deposition in a strong magnetic field [1)]

Crystal-oriented and crack-free thin TiO2 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. It was observed that the photo-current using the films depended on the plane orientation. (Fig. 2).

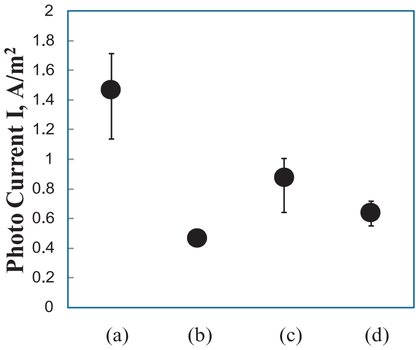

Fig. 2. Figure Photo current dependence of oriented TiO2 photoelectrodes; (a) c-plane of TiO2 parallel to ITO face; (b) preferential-orientation of (101) plane; (c) c-plane of TiO2 perpendicular to ITO face; (d) randomly-oriented film.

(2) Developement of Spark Plasma Sintering (SPS) [2)]

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. (Fig. 3) By increasing sintering pressure, complete densification was obtained reducing the peak temperature measured at die surface.

Fig. 3. Schematics of the punch/die mechanical contact: a) loose contact; b) close contact.

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Bio-inspired Nanostructures

MANA Principal Investigator **Zhong Lin WANG**
(Satellite at Georgia Tech, USA)

1. Outline of Research

Our project is focused on understanding new type of photonic structures provided by nature. Based on this, we plan to design some manmade photonic structures for real applications. *Morpho* Butterflies and *Jewel* beetles are the target biologies we chosen at present.

The bulk photonic properties are mainly determined by two key factors, the dielectric constant of the materials and the structural periodicity in one, two or three-dimensions, in another word, how the dielectric materials are stacked together. In nature, the diffraction index (the square root of dielectric constant) of bio-materials is close to 1.56, which is much lower than most inorganic dielectric materials. Therefore, the merit of bio-structure is their unique stacking sequences.

In order to understand the photonic structure of butterflies and beetles, our project was carried out from below directions.

1) Using electron microscopy to fully characterize the 3D structures. Measuring the reflectance spectra at different conditions.
2) Using MIT photonic-bands (MPB) software to fit the measured spectra.
3) Fabricating periodic manmade dielectric nanostructures to achieve designed photonic properties.

2. Research Activities

(1) The photonic structure of morpho butterfly wings

Cross-section and plane-view transmission electron microscopy (TEM) images displaying in Fig. 1 reveal the structure difference between the cover scale and ground scale of *morpho* butterfly wing. It is the denser packed bridges in between lamellas in ground scales.

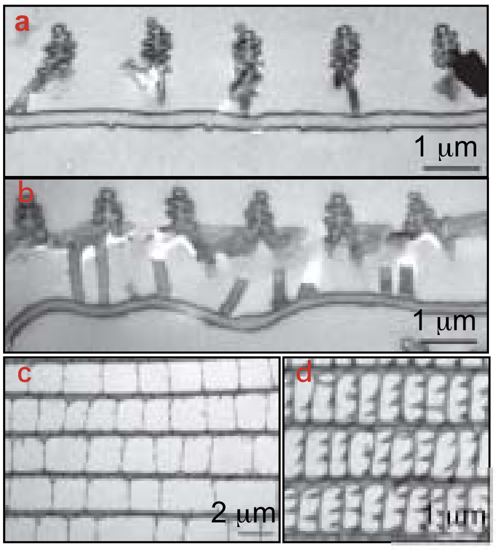

Fig. 1. Cross-section and plane-view TEM images of cover scale (a, c) and ground scales (b, d).

With incident light at normal direction and 20°, the scattered light appear at 30° and 50°, respectively, as showing in Fig. 2., which is a clear grating properties.

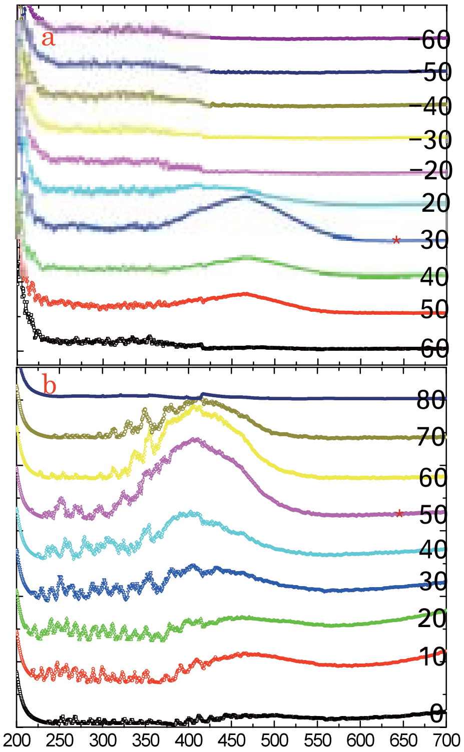

Fig. 2. Scattering spectra of ground scales at different exist angles with (a) normal and (b) 20° incident light.

At present, theoretical work is carried out to reveal how the coupling happened between cover scales and ground scales.

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Nano System Technology

MANA Principal Investigator **Masakazu AONO**
MANA Scientist Yuji Okawa, Makoto Sakurai
MANA Research Associate Hiromi Kuramochi, Hiroyuki Tomimoto, Genki Yoshikawa

1. Outline of Research

The goal of our research group is to create new nanosystems having novel functionality of interest using various key technologies of "materials nanoarchitectonics" and put the created nano-systems to practical use to contribute to our society in such forms as environmental and energy sustainability, next-generation computation and communication, and regenerative medicine.

To achieve this interdisciplinary research, we are making close collaboration with other groups in MANA as shown in Fig.1. We are also making active collaboration with other research groups outside MANA, i.e. the groups of Prof. Jim Gimzewski (UCLA, USA), Prof. Mark Welland (University of Cambridge, UK), Prof. Christian Joachim (CNRS, France), Prof. Christoph Gerber (University of Basel, Switzerland), etc. (all of them are Principal Investigators of the Nano-System Field of MANA).

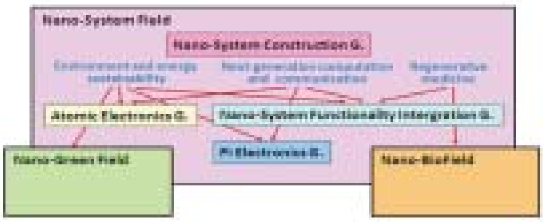

Fig. 1. **Collaborationof the Nano-System Construction Group with other groups in MANA.**

2. Research Activities

Our recent research activities are classified into the following five subjects:

1) Electrically wiring single functional molecules with single electrically conductive polymer wires.
2) Development and application of a novel scanning- probe method to measure nanomagnetism using no magnetic tip.
3) Atomic switch: 1) Practical use (commercializa- tion) of the atomic switch in programmable ICs (in collaboration with NEC) and 2) the application of the learning ability (memory effect) of the atomic switch to realize novel brain-type data processing devices.
4) Development of multiprobe scanning-probe microscopes and their application to the measurement of electrical conductivity at the nanoscale and to the analysis of signal transmission in neural networks.
5) Control of the polymerization and depolymerization of local fullerene (C_{60}) molecules only by changing the polarity of voltage applied to the local area.

In what follows, only 1) and 2) are discussed in more detail because of limited space.

We have developed a method[1-3] to create a single electrically conductive linear polymer chain (polydiacetylene) [4] at designated positions by initiating chain polymerization of monomers (diacetylene) using a scanning tunneling microscope (STM) tip. By using this method, we have tried to make two-terminal nanowiring for a single luminescent phthalocyanine molecule (see Figs. 2a and b) and succeeded in making such nano- wiring (see STM images in Figs. 2c and d).

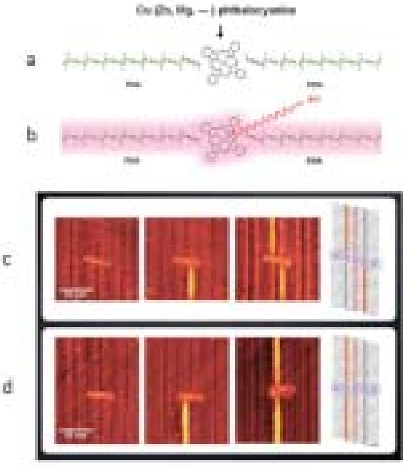

Fig. 2. **Wiring a single phthalocyanine molecule with conductive polydiacetylene molecular chains. Schematic figures (a, b) and STM images (c, d).**

We have developed a new scanning-probe method to measure nanomagnetism using no magnetip tip [5], which is based on the principle shown in Fig. 3. The method was successfully applied to measure the magnetic properties of nanometer-thick iron films on a GaAs substrate.

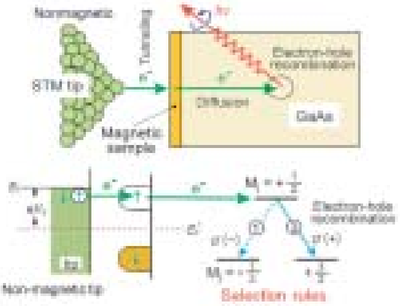

Fig. 3. **Principle of a developed novel method to measure nano- magnetism conveniently.**

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Extreme Field Nanofunctionality

MANA Principal Investigator Daisuke FUJITA
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MANA Research Associate Xinli Guo, Yinghui Yu, Jian-Hua Gao

1. Outline of Research

In the world at the nanoscale and moreover on the surface, where the dimensions are limited to two, one and zero, novel low-dimensional structures with unique physical properties may appear. By the manifestation of novel nanofunctionality in the low-dimensional world, the innovation towards new materials science can be expected. Nanofunctionality is thought to be derived from surface and/or quantum effects in addition to the size effects. Generally, it appears remarkably in the extreme field such as low temperature, high magnetic field and so on. Also, the control of the environments such atmospheres and elevated or lowered temperatures plays an important role in the creation of novel nanomaterials. Moreover, on the surface, combination with various environments can cause low-dimensional phases through a wide range of self organizations like adsorption, segregation, reconstruction and precipitation. Spontaneous change into the new phase may be possible by giving a perturbation with a nano probe in combination with self-organization phenomena. Thus, the research composed of self organization, extreme field, and nano probes is the main theme which we esteem.

Here, the research purpose is creating a progressive surface nanomaterials and searching their novel surface nanofunctionality by using the advanced nanoprobe technologies combined with extreme fields and self-organization. The possible outputs of the research are schematically shown in Fig. 1.

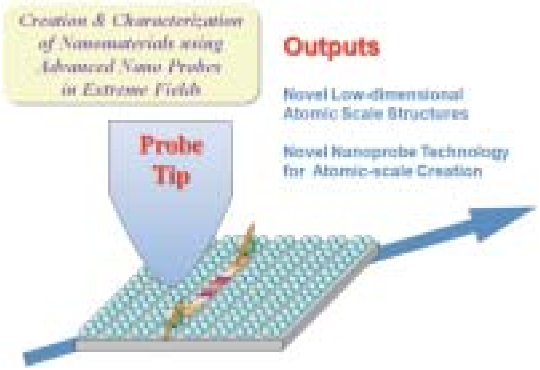

Fig. 1. Schematic image of the research methodology and the outputs.

2. Research Activities

(1) *Creation of Surface Nanostructures by Controlled Stress and Strain*[1)]

We have developed UHV scanning probe microscope with *in situ* external stress application to clarify the effects of stress and strain on surface atomistic structures. Controlling them will be a key technology for future nanofabrication processes.

Atomic resolution imaging under external tensile stress has been demonstrated on Si(111) and Si(001). Besides, domain redistribution induced by applying uniaxial stress on Si(001) has been successfully observed, as shown in Fig. 2. It suggests that it is feasible to fabricate single domain surfaces in a process that controls surface stress and strain.

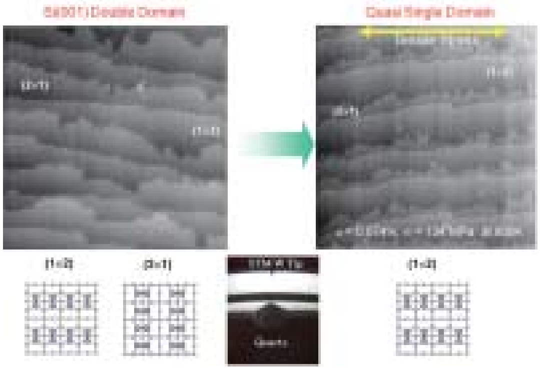

Fig. 2. STM observation with uniaxial tensile stress on Si(001) demonstrating the formation of quasi single domain.

(2) *Unusual mosaic image of the Si(111)-(7×7) surface coinciding with field emission resonance in STM*[2)]

Field emission mode with atomic resolution reveals an unfamiliar topographic image of a clean Si(111) surface, so-called mosaic patterns, within a narrow range of high sample bias coinciding with the field emission resonance. The mosaic patterns are found to be associated with the configuration of displaced center adatoms and adatom vacancies, induced by energetic electron injection, within the faulted half of the unit cell as shown in Fig. 3.

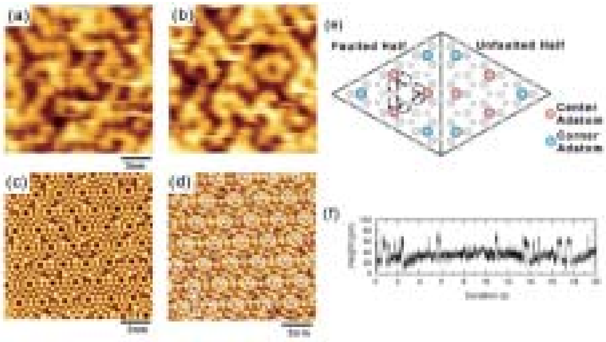

Fig. 3. (a) and (b): Consecutive FE-STM images of Si(111)-(7×7), exhibiting mosaic patterns at 79 K with *Vs*= +5.0 *V*. (c) and (d); STM images at *Vs*= +1.0 and 2.5 *V*, respectively, in the same area. (e); DAS structure model. (f); *Z* Piezo height recorded at Vs= +5.0 V. Variation between the two states is due to adatom displacement.

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MANA Brain: Atomic Neural Networks

MANA Principal Investigator **James K. GIMZEWSKI**
(Satellite at UCLA, USA)
Technical Director Adam Z. Stieg
Postdoctoral Scholar Greg Pawin
Graduate Student Carlin Hsueh, Haider Rasool

1. Outline of Research

We are developing a novel hardware-based neural network through a synergy of biological inspiration and advanced nano-electro-ionics using the memristive properties of the Aono atom-switch. In contrast to traditional approaches of neural network design that employ open circuit architectures and software design/ implementation, we will mimic the biological brain and synaptic interface through novel applications of atomic switching technology including, but not limited to, their incorporation into fractal nanowire networks. Pioneering work developed at NIMS in near-threshold ionic-resistive switching properties indicates strengthening phenomenon in the Ag/AgS junction system, analogous to processes that occur in the mammalian synapse. Depending on the polarity of the input signals, strengthening or weakening of a given synaptic connection can be achieved.

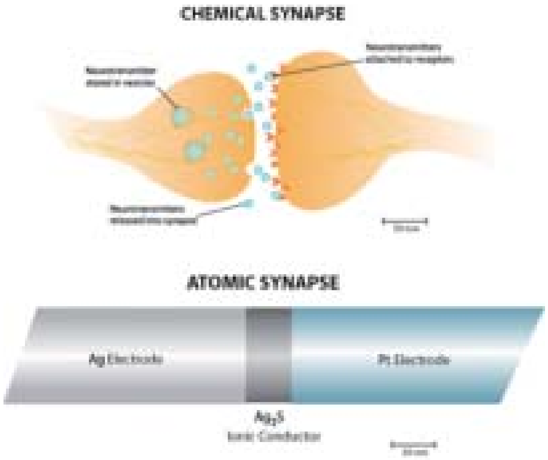

Figure 1. **Representative drawing of the biological inspiration for application of the Aono atom-switch as a synthetic synapse.**

Current work at the UCLA/CNSI MANA Satellite Laboratory involves three major research themes:

1. Elucidation of switching mechanisms through development and application of advanced scanning probe microscopies (SPM).
2. Examination of dimensional scaling effects at the switching interface.
3. Exploration of communication and network behavior within switching arrays.

2. Research Activities

(1) *Development of advanced SPM methods in UHV and electrochemical environments using nc-tuning fork and cantilever sensors with 10 fm noise interferometer. These will enable conductivity and atomic resolution topography of switching*

(2) *Growth of dendritic silver fractal networks from multiple electrodes with sulfurized interconnects. Deposition of atom switch network structures. (Figs 2 and 3).*

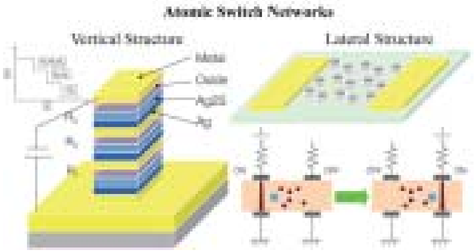

Figure 2. **Schematics of concept and synthetic approaches for the study of network behaviors in switching arrays.**

(3) *Electrical testing of: memristive properties, synaptic strengthening and weakening of networks, and evaluation of local changes with conductive atomic force microscopy (AFM) to establish best conditions for a neural learning system.*

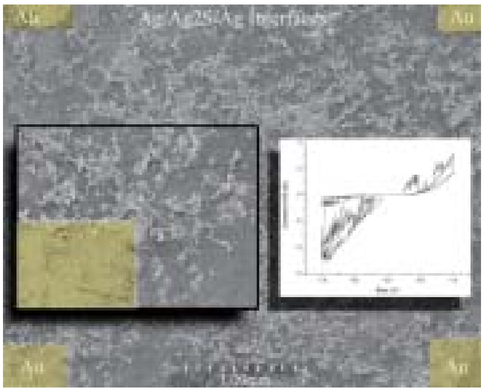

Figure 3. **Scanning electron micrograph of four-terminal network switching device fabricated by electroless deposition and subsequent electrical characteristics (inset).**

(4) *Exploration for oscillatory chemical and ionic behavior within networks. Evaluation of stability of silver networks and alternative platinum networks through electrochemical deposition using small copper spheres as silver nucleation sites for electroless deposition to create bridging links of silver which are then reacted with sulfur.*

Recent Publications with MANA recognition:

J. Reed, W. Walczak, O. Petzold, J.K. Gimzewski. *Langmuir* (in press/available online).

P.R. Wilkinson, W.S. Klug, B. Van Leer, and J.K. Gimzewski. *Journal of Applied Physics* **104**(10), (2008).

A. Z. Stieg, H. I. Rasool, and J. K. Gimzewski. *Review of Scientific Instruments* **79**, 103701 (2008).

Atomic Electronics for Future Computing

MANA Principal Investigator **Tsuyoshi HASEGAWA**
MANA Scientist Kazuya Terabe, Tohru Tsuruoka
MANA Research Associate Takeo Ohno, Shouming Wu,
Chuanbo Li, Yaomi Ito

1. Outline of Research

We aim to explore new nanosystems showing novel functions based on atomic electronics. The new nanosystems are expected to realize new computing systems such as by achieving fault tolerant logic circuits, nonvolatile logic circuits, optical and chemical sensors, and so on. Since the present-day semiconductor systems based on CMOS devices is approaching to their maximum performance due to the ultimate downsizing, new types of logic systems using beyond-CMOS devices should be developed for further progress in information technology. In this study, we will use the atomic electronic device, which has been developed by ourselves, for making new nanosystems. The atomic electronic device, such as atomic switch, is operated by controlling movements of cations and/or atoms in a nano-scale using nanoionics phenomena. 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 nonvolatile, 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 programmable device may be developed.

In order to accomplish the purpose, we will conduct 1) basic research on nanoionics phenomena, 2) developing new atomic electronics devices showing the novel functions based on the basic research, 3) developing nanofabrication technique for making the atomic electronics devices, 4) demonstration of novel operation of the atomic electronics devices and basic circuits using them. Figure 1 shows variety kinds of functions achieved by atomic electronics devices. In this study, these functions are utilized to achieve such as novel nonvolatile logic operation and neural networking systems.

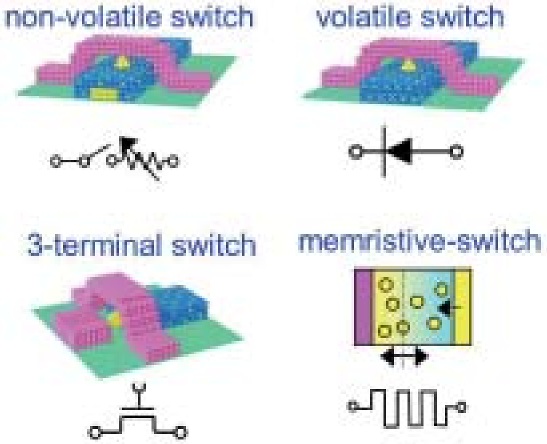

Fig. 1. Atomic electronics devices showing variety kinds of functions.

2. Research Activities

(1) Toward sub-20 nm hybrid nanofabrication by combining molecular ruler and electron beam lithography[1)]

The atomic electronics devices have structures of nanometer scale, which is a key factor to achieve novel functions. Therefore, nanofabrication methods must be firstly developed both for basic research and device development. We have succeeded in developing a new fabrication process for the atomic electronic devices by combining molecular ruler and electron beam lithography (Fig. 2). The method enables us to fabricate complex structures in nanometer scale for realizing variety kinds of atomic electronic devices such as shown in Fig. 1.

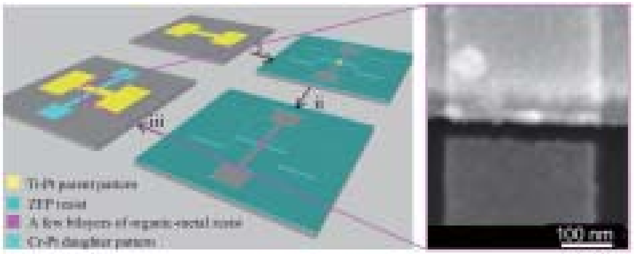

Fig. 2. Schematics of the newly developed nanofabrication process and a SEM image of the fabricated nanostructure.

(2) Atom Transistor[2)]

Nonvolatile three-terminal device is a potential device to realize nonvolatile logic. We have succeeded in demonstrating the three-terminal operation using $Cu/Ta_2O_5/Pt^2$ device structure based on the nonstoichiomety-induced carrier modification model, which we had developed for the two-terminal operation. By controlling the ionic movement using the gate electrode, the source and drain electrodes were successfully connected as shown Fig. 3. It can be turned off only by using the gate bias voltage. The results also open multi-terminal operation research for neural networking.

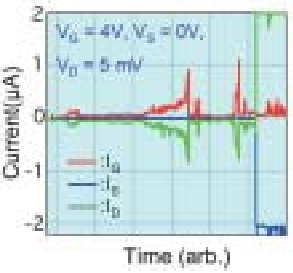

Fig. 3. Three –terminal operating result.

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Theoretical Study on Nano Materials and Novel Functions

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MANA Research Associate Yong Yang, Bin Liu, Shu-jun Hu
Graduate Student Shi-zeng Lin

1. Outline of Research

Paradigm shift is taking place in materials science. Instead of serendipity, designs of desirable electronic structures are expected to play pilot roles. The background of this trend is two-fold: First, the limited available resources and the already heavily damaged environments pose a constraint on new technologies and systems. Secondly, our knowledge and technology are advanced enough such that we are about to be able to put atoms and molecules at the desired positions and to predict the functions of the ensembles.

The main idea of the nano science and technology is to miniaturize devices and systems to the limits imposed by quantum mechanics, which reduces operation time, increases density of circuit integration, and minimizes energy consumption. However, it is well known that the Si-based electronics will shortly meet their ceiling in the direction of miniaturization. New breakthroughs in materials science are necessary in order to take up the grand challenge.

We focus on two major directions, namely the superconductivity and spintronics. As is well known, superconductivity is a macroscopic quantum phenomenon, and is unique since electric transportations take place at zero dissipation, superior to any other materials. To achieve superconductivity at higher temperatures is the most important goal of the research, which recently focuses on searching new Fe-based materials. Meanwhile, the phase of the superconductivity order parameter provides plenty of possibilities for development of novel quantum devices. A fantastic example is to develop a compact generator for continuous and frequency-tunable terahertz electromagnetic waves via the ac Josephson effect, which indicates that the superconductivity phase should evolve with time when the Josephson junction is subject to a dc voltage.

Spintronics is another very active research field, which aiming to control the spin degree of freedom of electrons simultaneously with the charge. As a most suitable material for spintronic applications, we recently focus on half metals, a class of materials which, due to the novel electronic structures, permit transportations of electrons with spin polarized in one direction. Our prescription is to make use of the couplings among the spin, charge, and orbital degrees of freedom in strongly correlated electron systems.

2. Research Activities

(1) *Discovery of a novel dynamic state of intrinsic Josephson junctions of cuprate high-T_c supercondutors*[1)]

Stimulated by a recent experimental breakthrough in excitation of THz electromagnetic radiation at a dc voltage bias on a thin mesa of BSCCO single crystal, we investigated the dynamics of superconductivity phase by the coupled sine-Gordon equations for the stack of intrinsic Josephson junctions. A novel dynamic state was found symbolized by a π phase kink (Fig.1), which explains all the important features observed so far in experiments, and indicates optimal conditions for strong THz radiations.

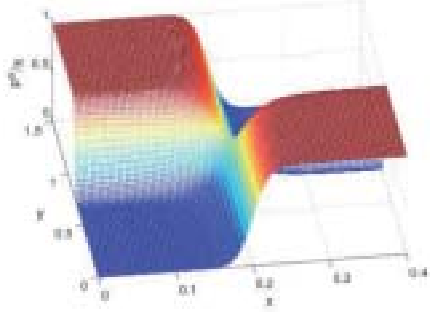

Fig. 1. π phase kink of the superconductivity phase in a rectangular mesa of the cuprate superductor BSCCO-2212.

(2) *Proposal of a half-metallic antiferromagnet via doping hole into an insulating ferrimagnetic cuprate*[2)]

From density-functional-theory calculations, we found that the spin of the hole doped into the new cuprate $Sr_8CaRe_3Cu_4O_{24}$ of perovskite structure is fully polarized due to the spin and orbital orders in the parent compound (Fig.2), which are established by the strong interactions among the electrons. The doped hole cancels out the spin magnetization of the parent compound, and simultaneously generates finite DOS in a single spin channel at the Fermi level, and thus renders a half-metallic antiferromagnet.

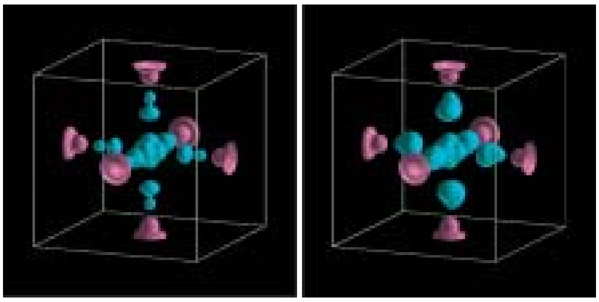

Fig. 2. Spin magnetization of $Sr_8CaRe_3Cu_4O_{24}$ (left) and the hole doped one with one of the 8 Sr atoms replaced by Rb (right).

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Atomic Scale Interconnects and Molecule-logic Gates

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1. Outline of Research

One fundamental question for the nanoscale is to determine the minimum number of atoms required to fabricate a calculating unit that is to assemble a nano-system which will be able to perform by itself a computation. Answering this question requires exploring at least 4 areas of science and technology:

- The quantum design of a molecule (or atom surface circuit) able to perform a logic operation,
- The molecule synthesis (respectively atom by atom UHV-STM fabrication on a surface) of the molecule logic gate (respectively the atom surface circuit logic gate),
- The invention of a surface multi-pad interconnection technology with a picometer precision respecting the atomic order of the surface nano-system assemblage.
- The development of specific quantum chemistry software able to reproduce the full logic gate nano-system functionalities with its interconnections and its supportive surface.

The GNS-CNRS Toulouse MANA satellite is working on 2 specific areas of this broad academic problem: the molecule synthesis of quantum logic gate with or without qubits (SWAP, NOR, AND gates) and the theory of surface electronics interconnects using surface atomic interconnections. We expect the understanding of the physics of surface interconnection using atomic wire of simple single molecule logic gate (or surface atomic circuit logic gate) to certify logic gate design and pursue the exploration of the molecule logic gate complexity roadmap to embed the maximum possible computing power inside a single molecule.

2. Research Activities

Finite length surface atom wire are one atom wide lines made either by constructing the wire atom by atom using STM lateral manipulation or by extracting atom by atom the passivation layer of a semi-conducting surface using STM vertical manipulation mode (see Fig. 1). In both case, those wires may reach a length of 20 up to 100 atoms. This means that the electronic band spectrum of the wire is not totally formed. Such an atomic wire is characterized by an electronic transparency made of a lot of molecular orbitals elementary electronic resonance.

The consequent peculiar pseudo-ballistic electron transport regime is now studied taking into account the elementary electron transfer events building up the current intensity. This time dependent problem is never tacked in atom or molecule device especially taking into account the environment (stray capacitance, electromagn. coupling…).

Starting from the time dependent electron transfer theory occurring between 2 reservoirs interacting via a super-exchange mechanism, we have proposed propose to develop a theory able to give in average the current intensity and its second moment, the noise spectrum of the junction 1).

We are now exploring this theory by first adapting the N-ESQC semi-empirical code able to calculate the electrical characteristics of the circuit Fig.1.

A single molecule logic gate can designed in a qubit or in an intramolecular electron transfer quantum interference approach. In both cases, the molecule (or the surface atomic circuit) is going to be implemented on a passivated semi-conductor surface (Fig. 1).

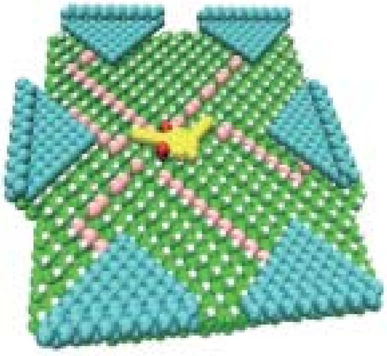

Fig. 1. A possible surface implantation of a molecule XOR logic gate interconnected using surface dangling bond atomic wires.

For a qubit mono-molecular approach, we are developing single molecule magnetism using localized spin stabilized inside a single molecule chemical structure to perform a logic operation whose computation can be trigger by a spin polarized STM experiment. The collaborative work with MANA-NIMS must first certify that the spin polarized STM technique is able to image the localized spin on a simple mixed valence organic complex synthesized in MANA Toulouse.

For the Quantum Hamiltonian Computing (QHC) molecule logic gate approach 2), the design is based on extremely simple conjugated organic board terrylene and pentacene derivative equipped with 2 lateral switchable by STM donor or acceptor groups. Those lateral group are going to be adapted as a function of the adsorption of the molecule on the atomic wires used for the interconnects. The collaborative work with MANA-NIMS is first targeted toward the fabrication of surface atomic scale circuit on a self passivated semi-conductor surface.

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Superconducting Quantum Nanoarchitechtonics

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1. Outline of Research

Our objective in this research plan is to develop new concept of materials science (Nanoarchitechtonics) especially in the field of superconductivity making use of modern nanotechnology in the ultimate quantum regime of materials. The challenge to study on the dynamical nature of the intrinsic Josephson junctions with and without magnetic field has been set forth by choosing high T_c superconductor $Bi_2Sr_2CaCu_2O_{8+\delta}$, which can be grown by us in a highest quality of single crystal form available in the world. June in 2007, a remarkable phenomenon, which has never been observed before, was discovered in the mesa of this material: strong, continuous and coherent electronagnetic waves at a terahertz frequency range was detected and the spectrum was analized by spectrometer. This achievement has made excitement in the community because this technology may bring the first full solid state THz devices potential for the vast important applications.

2. Research Activities

We have succeeded in generating intense, coherent and continuous THz electromagnetic waves from mesa structures made of high quality single crystal of high T_c superconductor $Bi_2Sr_2CaCu_2O_{8+\delta}$ well known as a series stack of intrinsic Josephson junctions. The mesas has the rectangular shape with a dimensions of 40~100 μm in width, 300~400 μm in length and 1~2 μm in thickness. It can be fabricated by FIB (Focused Ion Beam) or Argon ion milling technique. The frequency of the emission is identical to the *ac* Josephson frequency of the single junction: $\nu=2ev/h=2eV/h=K_JV$, where v is the voltage appearing between two electrodes of the single junction, $V=N\nu$ the total voltage of the mesa, e the elementary charge, N the total number of the intrinsic Josephson junctions and h the Planck's constant[1]. From our experimental results we have established another important condition for the emission: $\nu=c_0/n\lambda=c_0/2nw$, where c_0 is the velocity of light in vacuum, λ the wave length of the THz wave generated in the mesa, n the refractive index of the mesa. This condition strongly implies that the mesa itself plays a very important role as the cavity resonator where the standing of wave with $\lambda=2w$ is set up.

The physical principle of oscillation can be understood as follows (see Fig. 1). When the mesa is current-biased, and exceeds the critical current, I_c, the branching effect characteristic of multi-stacked Josephson junctions happens to occur. Further increasing the current makes the mesa to the full voltage state, where all junctions are in resistive state. Since the resistance at this state is large, the heat generated in the mesa reaches to several 10 kW/cm^3. Therefore, the mesa may get heated severely and the temperature is easily expected to exceed even to the normal state above T_c. The typical *I-V* curves in this regime are demonstrated in Fig. 1(right).

When the current is reduced, the heating is also reduced, and the mesa becomes the superconducting state, where the *I-V* curve shows a large hysteresis behavior. When the current is further reduced and two conditions mentioned earlier are fulfilled at a certain voltage, the emission occurs. The detector signal is also shown in Fig. 1(red line). It is noted that the emission power has strong temperature dependence having a maximum between 20 and 40 K, and it ceases at the rest of temperature region. This very peculiar behavior strongly suggests that heating which may cause the nonequilibrium state in the mesa may play an essential role for the oscillation.

Recently, a great effort has been made to determine the electromagnetic modes of standing of waves inside the mesa. The result can be compared with the recent theoretical works done by numerical simulations. Furthermore, the computed results can be fed back for the designing of the mesa in order for improvement of efficiency of the radiation.

At the present stage, the total power estimated is approximately 5 μW, being proportional to N^2. The efficiency of the emission can be estimated to be about 10^{-4}, which seems to be too low. Our next task is to improve efficiency as high as possible.

This work has partly been done by the international collaboration with Dr. Wai -K. Kwok group at Argonne National Laboratory, USA.

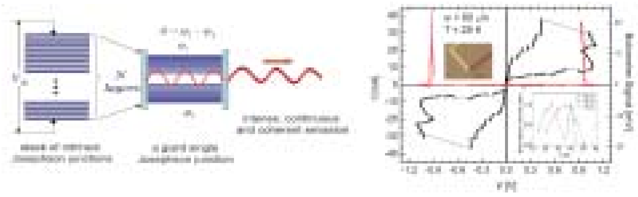

Fig. 1. The principle operation: a giant electromagnetic wave oscillation takes place in the mesa of an intrinsic Josephson junction similar to LASER (left). The typical *I-V* curve of the mesa. The strong radiation is observed at a certain voltage represented by red line (right).

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[1] The constant K_J is called as the Josephson constant and has a value of 0.483597891 ± 0.000000012 (THz/mV). This K_J is also equivalent to the reciprocal of quantum flux ϕ_0: $K_J=1/\phi_0$.

Integration of Nano Functionality for Novel Nanosystems

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Katsumi Nagaoka, Osamu Kubo
MANA Research Associate Liping Zhao, Shin Yaginuma, Masato Nakaya

1. Outline of Research

We are developing and exploiting novel techniques and methodologies toward the realization of novel nanosystems for future information technology. Different types of research topics, such as development and application of a multiple-scanning-probe microscope (MPSPM), manipulation of individual atoms and molecules, and measurements of signal transfer through living cell systems, are explored for a common purpose; creation and characterization of elemental and organized nanostructures which transmit and transduce electrical, optical, mechanical, ionic and magnetic signals.

MPSPM is an instrument which has simultaneously and independently controlled 2 to 4 probes. Those probes are brought in electrical contact to a single nanostructure to investigate its electrical property[1,2]. We have measured electrical resistances of films of fullerene C_{60} molecules[3], single rare-earth metal silicide nanowires self-organized on Si(001) [4,5], single-walled carbon nanotubes and so on.

Fabrication of nanostructures by means of self-organization[6,7], atom/molecule manipulation[8] and dynamic shadow mask deposition[9] is also pursued because such nanostructures and processes are keys to realize meaningful nanosystems.

A nerve cell and a network of the cells are sophisticated hierarchical materials systems which are known to ultimately device a human brain. As we believe that the working principle of such a cell system gives a breakthrough to the present computing technology, considerable efforts are devoted to investigate signal transfer and transduction through single and conjugated living cells (see Fig. 1) in collaboration with the Biomaterials Center of NIMS. Here, we again use our MPSPM and related techniques to understand the signal transfer from nanoscopic viewpoints.

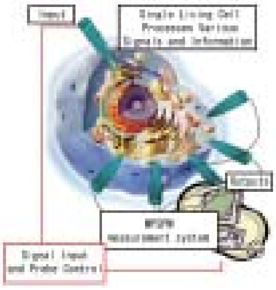

Fig.1. Schematic illustration of a "cell odyssey" using the MPSPM which works in liquid environment.

2. Research Activities

(1) Multiple-scanning-probe Microscope[1-5]

Our MPSPM systems to investigate electrical properties of nanostructures revealed interesting properties of various nanostructures and nanomaterials; metallic behavior of fullerene polymer, electron scattering in nanowires and at the nanowire/substrate interfaces and ballistic transport of electrons through nanowires. Figure 2 shows an example of the electrical resistance measurements of a single nanowire of $ErSi_2$ on Si(001).[4]

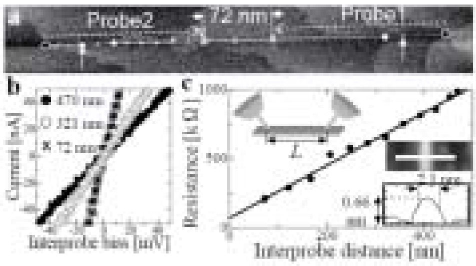

Fig. 2. Electrical resistance measurements of a single $ErSi_2$ nanowire using our double-scanning-probe type MPSPM.

(2) Controlling reversible intermolecular reaction for data storage[8]

Demands for high-density data storage is increasing. We have found that the transformation between monomers and a dimer (or trimer) of C_{60} can be surprisingly well-controlled by a sharp probe of SPM at room temperature. As shown in Fig. 3, this control can be done reversibly thus applied for future data storage with a bit density of more than 100 Tbits/in^2.

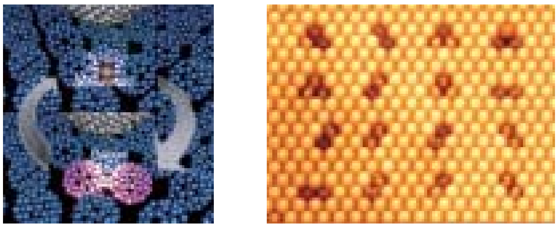

Fig. 3. Left panel: Schematic illustration of intermolecular chemical reaction controlled by STM. Right panel: Array of bits recorded in a thin film of C_{60} using the controlled intermolecular reaction.

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Mesoscopic Superconductivity and Quantum Information Physics

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1. Outline of Research

Our research topic is so-called mesoscopic super- conductivity which aims to explore new quantum phenomena in different kind of superconducting devices and to apply them to quantum information physics. We are now working mainly on two following subjects.

(1) Nano-SQUID

We will develop an ultimate SQUID (Superconducting Quantum Interference Device), i.e., a nano-SQUID which can detect single or several spins. As to the limit of time resolution measurement, we will develop a nano-SQUID that detects a single spin flip in 1 Hz and the relaxation process of several spins in 10-100 MHz order. We will also clarify the quantum interaction between a nano-SQUID with embedded quantum dots or graphene sheets and spins in dots or sheets (Fig. 1). This leads to the implementation of an entangled state between a superconducting qubit and spin qubit. The combination of these qubits is a promising candidate for a quantum interface that will be indispensable in the future quantum information network.

(2) Ferromagnetic-semiconductor/superconductor junctions

It is clear that spins from an F (ferromagnet) can penetrate into an S (superconductor) in an S/F junction with a good contact from the viewpoint of spin injection. This spin injection effect thereby affects the properties of a superconductor. It is called the inverse proximity effect. We are going to investigate this effect using a ferromagnetic-semiconductor/superconducting junction (Fig. 2) and clarify the quantum phase coherence of injected spins into S.

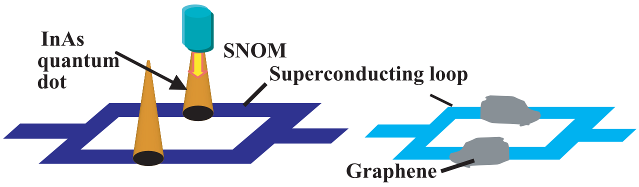

Fig.1. Nano-SQUIDs with embedded quantum dots (left) and graphene sheets (right).

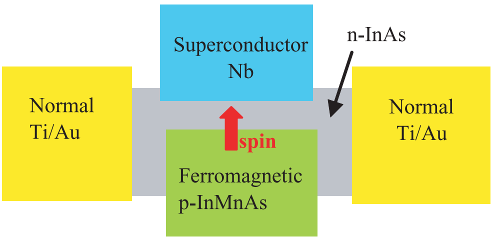

Fig.2. Schematic diagram of a Nb(S)/n-InAs(N)/p-InMnAs(F) junction.

2. Research Activities

(1) Discovery of two-photon-driven level anticrossings in the SQUID qubit-resonator system[1)]

We had a clear evidence for the coexistence of one- and two-photon-driven level anticrossings in the flux-Qubit (DC SQUID) coupled with a resonator. Our experiments and theoretical analysis shed new light on the fundamental symmetry properties of quantum bit circuits and the non-linear dynamics inherent to circuit QED (Quantum Electrodynamics).

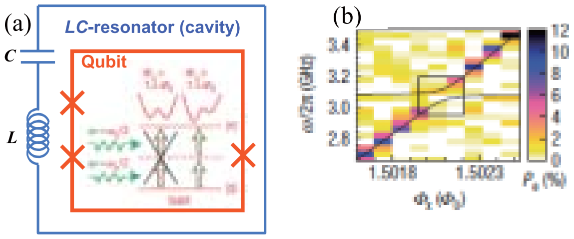

Fig. 3. SQUID qubit-resonator system. (a) Two-photon process occurs in the coupled system and (b) anticrossing under two-photon driving measured in the probability to find the qubit in the first excited state. *y* and *x* axes are driving frequency and flux bias, respectively.

(2) Spin-polarized Carrier Injection Effect[2)]

We have measured the transport properties of a n-InAs channel/ which has connections with p-InMnAs and Nb, where a p-InMnAs can be regarded as a spin injector (Fig. 2). The differential conductance of n-InAs channel as a function of bias voltage showed different behaviors against current injection (Fig. 4). We found that spin-polarized current from InMnAs induced the exchange field in the Nb electrode and the so-called inverse proximity effect could explain the difference of the conductance behaviors measured in experiments.

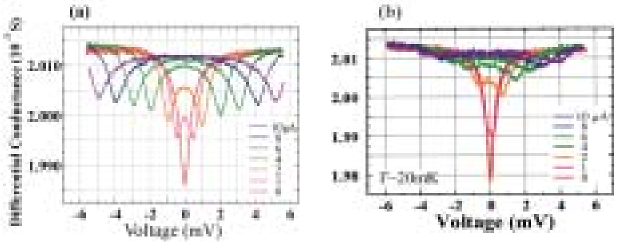

Fig. 4. The bias voltage dependence of the differential conductance of the n-InAs channel as a function of injection current (a) from Nb and (b) from p-InMnAs at 20 mK.

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Surface Control for Organic Transistor

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MANA Scientist Takeo Minari

1. Outline of Research

Since the field effect mobility of organic field-effect transistors OFETs has reached that of amorphous silicon based transistors, practical applications are now being considered. Several features of OFETs are expected to provide the wide scale applications based on large-area and flexible electronics. On the other hand, significant advantages have not been established for the manufacturing process of OFETs, which still require similar techniques as that used for silicon-based electronics. Furthermore, organic transistor based on the self-assembled molecule film has so many issues at various interfaces. Unclear interfaces are as follows: (1) metallic contact/organic film, (2) gate-insulator/organic film, (3) grain boundary connection in the organic film, (4) molecule-molecule interface with p-electron overlapping, and (5) organic film/passivation film. None of them are fully clarified to stabilize the transistor operation and to design up the electric circuit. For instance, very high contact resistance, operation threshold voltage, and on/off ratio, that are correlated to the interfaces, are still uncontrollable. Instability and non-reproducibility of the device cause serious delay in research and development of the organic transistor..

We have investigated these above issues to realize the practical organic transistors. The physics behind the issues and the control method developed will generally be applicable to the π-electron electronics. [1-3]

2. Research Activities

As a one of our resent progresses, a surface-selective deposition for selective organization control of organic transistor formation was succeeded (Fig.1). This technique is based on patterned functionalities on gate-insulator 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 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. 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 transistor characteristics with remarkable high reproducibility were achieved in the self-organized channel.

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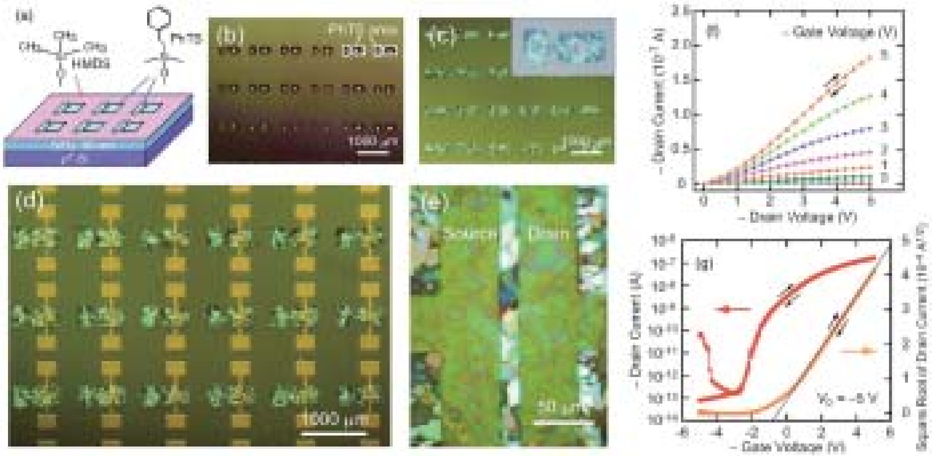

Fig.1. Fabrication process and electrical characteristics of self-organized arrays of OFETs. (a) Schematic of a silicon dioxide substrate patterned with two SAMs having different wettability for the solvent. (b) Drop casting of an organic semiconductor solution yields small droplet arrays aligned on the wettable PhTS area. The PhTS area is indicated by a white line. (c) As the solvent evaporates, the organic semiconductor films are self-organized on the selected area. The inset shows a magnified image of an individual pattern. (d) Arrays of polycrystalline transistors integrated by the self-organization technique. Several tens of devices were simultaneously formed from a solution phase. The channel length and width are 20 and 300 μm, respectively. (e) Polarized optical micrograph of an 8QT8 transistor around the channel region. High crystallinity of the solution-processed film is indicated. (f) Output and (g) transfer characteristics of a typical polycrystalline device.

Bio-inspired Materials for Sustainable Energy

MANA Principal Investigator **Mark WELLAND**
(Satellite at Univ. Cambridge, UK)
David Bowler
Graduate Student Rami Louca Morgan, Conn O'Rourke,
Umberto Terranova

1. Outline of Research

We are investigating the electronic and mechanical properties of materials based on biologically-inspired charge transfer molecules and complexes. We will use a combination of self-assembly and directed assembly via lithography to create appropriate structures, taking our inspiration from biological systems. The work started in October 2008 in Cambridge (PhD student Rami) and in January 2009 in UCL (PhD students O'Rourke and Terranova). The experimental work will consider both single molecules and their electronic properties and larger scale structures and their mechanical properties and assembly; this will take place in Cambridge. The modelling programme will be based on the Conquest linear-scaling DFT code (developed jointly by UCL and NIMS) and will investigate the structural and electronic properties, and extend the code to consider electron transfer and excited states via cDFT and TDDFT; this will take place in UCL. We will jointly develop methods for investigating charge transfer and photoexcitation in these materials. David Bowler will continue to work in Nanoscience in Cambridge at least one day a week (as he has done as part of the IRC in Nanotechnology) in order to provide the primary link for collaboration between the two teams.

2. Research Activities

Theory Density functional theory (DFT) has become the standard method for understanding the properties of materials from first principles. Normal DFT techniques scale badly with the size of the system studied (the computer effort increases with the cube of the system size, while memory required increases with its square). The Conquest code [1)], which was developed with NIMS, scales linearly with system size (and also works extremely well on massively parallel computers). This makes it the ideal platform for DFT studies of nano-scale systems. However, when applied to the important problem of charge transfer, DFT often produces inaccurate results; the technique of constrained DFT, which we are implementing in Conquest, can be used to correct these inaccuracies. For molecular energy levels (often key in charge transfer problems) we will use the method of time-dependent DFT or TD-DFT.

We will consider the problem of dye molecules on MgO, TiO2 and ZnO substrates. Initially we will characterise the dyes in gas phase, moving to the more challenging problem of surfaces later. We will generate simulated STM images of the dyes for comparison with experiments, and will look at the effects of charge excitation on atomic and electronic structure of the dyes in gas phase, in solution and on substrates.

Experimental. Rami Morgan will initially build on existing work at Cambridge to synthesise nanowires of ZnO and TiO2 using wet chemistry based processes. The process produces a highly oriented array of nanowires that nucleate on a thin insulating layer on ITO. The next step, as we have previously done with our ZnO system is to spin on a mixture of conducting polymer and dye molecule to effect exciton generation. At this point the theory will start to dictate whether what type of nanowires we use, and what the optimum dye molecule is dependent upon band gap energetic and carrier lifetimes. We will then use a set of different experimental methods to determine the physics of the charge separation process so as to optimise PV efficiency. A guiding principle of the experimental work will be to ensure that we concentrate on processes that are scalable and truly manufacturable; we will not look at unrealistic systems no matter how efficient they may be.

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Construction of Interfacial Phases with Atomic/Molecular Order for Highly Efficient Conversion of Energy and Materials

MANA Principal Investigator Kohei UOSAKI
(Satellite at Hokkaido Univ., Japan)

1. Outline of Research

One of the most challenging problems for chemists/ material scientists is construction of efficient energy/ materials conversion systems. In natural systems, solar energy is efficiently converted to chemical substances with high energy and chemical substances are efficiently converted to work and other compounds utilizing 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 and the efficiency and durability of these systems are still needs to be improved.

In this study, we would like to establish techniques to construct interfacial phases for highly efficient energy/materials conversion, mainly at solid/liquid interfaces, by arranging metal, semiconductor and organic molecules with atomic/molecular resolution. Furthermore, the detailed *in situ* analyses by STM and non-linear spectroscopy of the structure and functions of the interfaces as well as theoretical study are carried out so that structure-function relations are established and rational design and construction of the desired interfacial phases become possible. Specifically, we carry out 1. construction of catalytic interfaces by atomically ordered modification of metal surfaces with foreign metals, 2. construction of photoenergy conversion interfaces by molecularly ordered modification of semiconductor surfaces, and 3. experimental and theoretical investigations of interfacial electron transfer processes.

2. Research Activities

(1) Construction of catalytic interfaces by atomically ordered modification of metal surfaces with foreign metals[1)]

Development of highly dispersed atomically controlled alloy particles attracted considerable attention because catalytic activities depend on the composition and structure of the alloy and efficient utilization of atoms requires high dispersion. For example, the atomic ratio giving maximum catalytic activity for electrochemical methanol oxidation reaction, one of the most important reactions in fuel cell, is suggested to be $Pt_{50}Ru_{50}$. It is, however, not easy to prepare alloy catalysts with ordered atomic level arrangement. Usually two metal sources, metal containing salts, are mixed together and decomposed thermally to obtain alloy. In this case, bulk ratio can be controlled but not nano-scale arrangement.

Here, we employed a new method, in which multinuclear metal complex is adsorbed on a substrate and then decomposed thermally/electrochemically so that atomically arranged nano-alloys can be formed as shown in Scheme 1. Recent study using Pt(II)-Ru(II) binuclear complexes showed that they adsorbed on gold(111) electrode surface in ordered manner and subsequent decomposition of the adsorbed species by heating followed by electrochemical treatment resulted in highly dispersed PtRu particles on the surface, giving remarkable increase of electrocatalytic activity for hydrogen evolution and methanol oxidation reaction.

Scheme 1. Construction of atomically arranged nano-alloy catalysts.

(2) Construction of Photoenergy Conversion Interfaces by Molecularly Ordered Modification of Semiconductor Surfaces[2)]

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. We have shown the efficient PEC hydrogen evolution at p-Si(111) electrode modified with multi-molecular layers with viologen (molecular wire) and Pt nanoclusters (hydrogen evolution catalyst).

(3) Experimental and Theoretical Investigations of Interfacial Electron Transfer Processes[3)]

To construct interfacial phases for highly efficient energy/materials conversion, it is essential to understand the mechanism of the interfacial reactions in general and interfacial electron transfer reaction in particular. Since electron probe techniques such as LEED, which are most commonly used for surface characterization in vacuum, cannot be applied to solid/liquid interfaces, various non-traditional techniques must be utilized. We have been using a wide range of techniques such as STM, AFM, SXS, XAFS, and non-linear optical spectroscopy. Recently, we have investigated potential dependent interfacial structures of water at Au and Pt electrodes using sum frequency generation (SFG) spectroscopy, which is an interface specific vibrational spectroscopy and found that water at Pt surface is more highly ordered and SFG intensity became minimum at potential of zero charge in both cases.

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High Performance of Organic Solar Cells

MANA Principal Investigator **Liyuan HAN**
MANA Scientist Ashraful Islam
MANA Research Associate Steffan Cook, Shang Gao

1. Outline of Research

We aim to develop new and promising technologies for the next generation of photovoltaic power as alternatives to traditional silicon solar cells. The main focus of our research will be on recent but already established research topics such as small molecule/polymer solar cells and dye-sensitized solar cells (DSC). Recently we have reported a newly structured DSC, called a back contact-DSC (BCDSC).[1] An intensity modulated photovoltage spectroscopy (IMVS) study indicated that the lifetime of electrons in the TiO_2 film of the BCDSC is long enough for efficient electron collection. We found that the back contact structure can be applied to DSCs even though mesoporous nanocrystalline, like grain boundary in polycrystalline silicon film, has many interfaces.

In the field of small molecule/polymer solar cells and dye-sensitized solar cell we aim to establish:

- An understanding of key parameters determining the operation efficiency of the devices, like electron transport properties in mesoscopic nanocrystalline metal oxide films and charge recombination process at P3HT/PCBM, mesoscopic oxide films and dye-coated oxide /electrolyte interfaces through investigation of transient absorption spectroscopy and impedance analysis.
- Begin study of new materials and experiment with new possible device architectures, such as inverse or tandem cells that can overcome some current challenges facing organic solar cell efficiencies.

In addition to the fabrication and characterization work here at NIMS in a collaboration with The National Institute for Advanced Industrial Science and Technology (AIST) we set out to also do a range of more fundamental studies on material properties and on charge generation and recombination mechanisms in the active organic solar cell layers. Such studies will use powerful optical pump-prope techniques to monitor electrical charge formation and decay on timescales of femto to milliseconds. Combined fundamental and device studies will hopefully allow us to assess correctly the weaknesses of our devices so that we can take appropriate future steps.

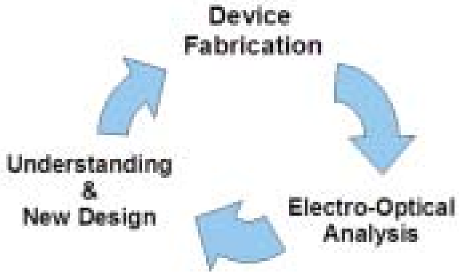

Fig.1 Research and development feedback cycle.

2. Research Activities

(1) Conjugated Polymer P3HT Material Studies: Exciton Diffusion Lengths.

We resolve the exciton diffusion length for P3HT via a time-resolved emission spectroscopy technique (see Fig.2). At low excitation laser powers decay of photo-generated excitons is mono-molecular (see Eq.1) leading to a straight line decay for emission with time on a log-lin plot. As the laser intensity is increased however, more emission from the sample is observed as more singlets are created but also the introduction of a quicker component to the emissive decay at early times. This quicker decay comes from the destructive collision of excitons (see Eq.2), and the speed of exciton diffusion can be known by analysis of the rate of collision. Hence exciton diffusion lengths was estimated to be over 20nm.

$$S^1 \rightarrow S^0 + h\nu \tag{1}$$

$$S^1 + S^1 \rightarrow S^1 + S^0 \tag{2}$$

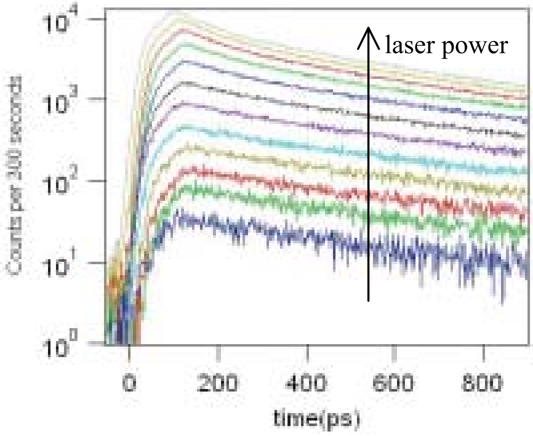

Fig. 2. Time-resolved emission data from films of P3HT with increasing laser illumination intensity (0.23-340x10^{11} photons pulse^{-1}cm^{-2}).

(2) New Device Structure of dye-sensitized solar cells

Studies are beginning to design a new device structure of dye-sensitized solar cells based on the modification of the chemical composition and material shape/order. Fundamental studies on electron and hole transport properties in mesoporous TiO_2 film and solid hole conducting materials, respectively, are under investigation.

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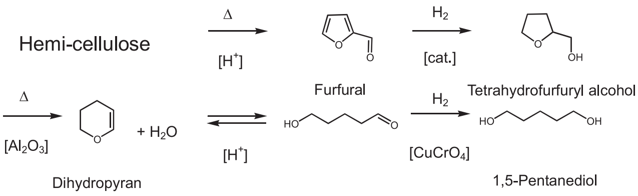
Catalyst Development for Biomass Conversion to Fuels and Value-added Chemicals

MANA Principal Investigator Keiichi TOMISHIGE
(Satellite at Univ. Tsukuba, Japan)
Graduate Student Shuichi Koso

1. Outline of Research

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, have been used as monomers for production of polyesters and polyurethanes. Development of catalysts and catalytic reaction for the production of terminal-diols from renewable resources has been needed, and one candidate among the terminal-diols is 1,5-pentanediol. It has been known that this 1,5-pentanediol is formed by hydrogenolysis of tetrahydrofurfuryl alcohol. Tetrahydrofurfuryl alcohol is one of the derivatives from furfural, which has been produced by acidic degradation of hemicellulose contained in agricultural raw materials abundantly. However, the selectivity to 1,5-pentanediol was low, and 1,2-pentanediol tends to be formed more preferably than 1,5-pentanediol over conventional hydrogenolysis catalysts. This low selectivity to 1,5-pentanediol is regarded as the limit of heterogeneous catalyst systems for hydrogenolysis, although heterogeneous processes have merits in terms of the separation of catalysts from products and reuse of catalysts. It has been proposed that 1,5-pentanediol is produced via dihydropyran and δ-hydroxyvaleraldehyde from tetrahydrofurfuryl alcohol achieving 70% yield as described below.



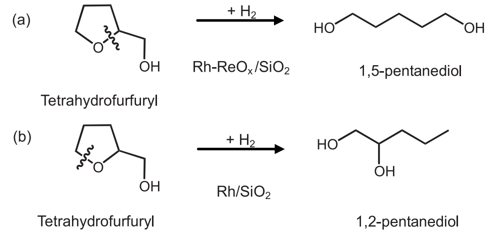
This method circumvents the hydrogenolysis with low selectivity, but three steps with isolation and purification of the intermediates by distillation are needed.

Purpose of our research is to develop a heterogeneous catalyst for the production of 1,5-pentanediol by chemoselective hydrogenolysis of tetrahydrofurfuryl alcohol. We found that Rh-ReO_x/SiO_2 is much more active and selective in the hydrogenolysis of tetrahydrofurfuryl alcohol to 1,5-pentanediol than conventional hydrogenolysis catalysts[1].

2. Research Activities

(1) High activity and chemoselectivity of Rh-ReO_x/SiO_2 in the hydrogenolysis of tetrahydrofurfuryl alcohol[1]

The modification of Rh/SiO_2 with ReO_x enhanced catalytic activity and selectivity of drastically. At the optimum amount of Re addition (molar ratio of Re/Rh=0.5), the activity of Rh-ReO_x/SiO_2 was about 10 times as high as Rh/SiO_2. Highest yield on the Rh-ReO_x/SiO_2 was 86%. The yield of this simple and single-step process is much higher than that of the multi-step process. Another interesting point is that a main product of Rh/SiO_2 is 1,2-pentanediol, in contrast, 1,5-petanediol is selectively formed over the Rh-ReO_x/SiO_2 as shown below.



(2) Structure of Rh-ReO_x/SiO_2[1]

Fourier transforms of Re L_3-edge EXAFS of Rh-ReO_x/SiO_2 after the reaction is shown in Figure 1.

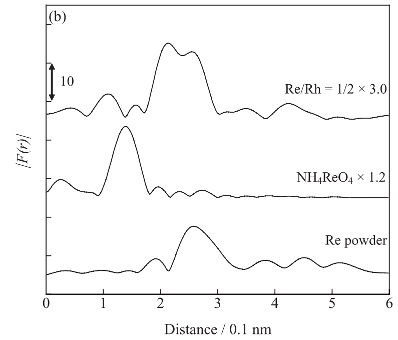
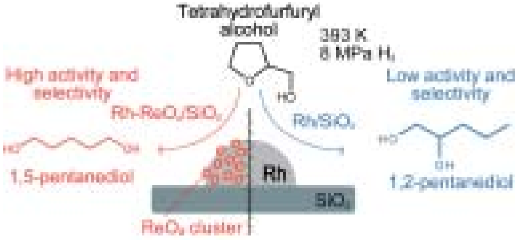


Fig. 1. Fourier transforms of Re L_3-edge EXAFS: Rh-ReO_x/SiO_2 and the reference compounds. FT range : 30-120 nm^{-1}.

Curve fitting results indicate the presence of the Re-Rh bond at 0.268 nm as well as the Re-O and Re-Re bonds. Rh *K*- and Re L_3-edge EXAFS suggest that Rh metal particles are formed and ReO_x clusters attached on the surface of Rh metal particles. Model structure of Rh-ReO_x/SiO_2 and Rh/SiO_2 and the reaction scheme is illustrated below.



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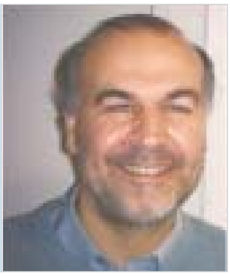
Nanostructured Materials for Solid Oxide Fuel Cells

MANA Principal Investigator **Enrico TRAVERSA**
MANA Scientist Emiliana Fabbri, Daniele Pergolesi



1. Outline of Research

Fuel cells are promising for sustainable production of energy given their low environmental impact and high chemical-to-electrical energy conversion efficiency. Solid oxide fuel cells (SOFCs), among the various fuel cell technologies, are the most promising for stationary energy production since they operate at high temperatures (ca. 1000 °C), but cost and durability are the main obstacles for SOFC mass use.

One of the major goals in SOFC research is reducing the operating temperature down to 700°C or less. Different approaches are followed for lowering SOFC working temperature. One major issue is the development of solid electrolytes with sufficiently high oxygen ion conductivity. Alternatively, ohmic resistance of the electrolytes can be decreased by reducing their thickness. Reduced operation temperature allows the development of miniaturized SOFCs for portable unit power generation, which need the use of thin-film electrolytes. Micro-SOFCs can produce energy densities per volume and specific energy per weight up to four times larger than state-of-the-art batteries.

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, and the use of nanostructured materials is extremely useful for this aim.

High temperature protonic conductors (HTPCs) also possess suitable conductivity as electrolytes in the 350-600 °C temperature range, coupled with low activation energy for proton conduction (0.3-0.6 eV). Moreover, for HTPCs water vapour is formed at the cathode side and not at the anode as for oxygen ion conductors, avoiding fuel dilution that reduces the cell efficiency. However, Y-doped barium cerate (BCY), the best proton conductor up to now, is chemically unstable in SOFC operating conditions, while Y-doped barium zirconate (BZY) is chemically stable with CO_2 and H_2O, but its conductivity is hindered by blocking grain boundaries. One of the challenges of the research related to SOFC using HTPCs is thus represented by the development of new protonic ceramics that would merge chemical stability with high proton conductivity. A solution is the development of a BZY-BCY bilayer structure, where a thin BZY layer act as a protective layer for BCY without affecting its proton conductivity 1).

In addition, suitable electrode materials need to be found to improve the performance of fuel cells based on HTPCs. For instance, the cathode materials studied until now are mainly the same materials used for oxygen ion conducting electrolytes, and little effort has been made to study specific mixed protonic-electronic conductors.

Aim of the MANA research project is the fabrication of micro-SOFC devices, starting from the understanding of the performance of nanostructured materials as single components or in assemblies.

Pulsed laser deposition (PLD) is a very promising technique for the fabrication of tailored oxide thin films for SOFCs, because it allows to obtain single crystal or polycrystalline films, with tailored microstructure from dense to highly porous, as shown in previous works 2).

The project aim will be pursued in different research steps, as the following:

(i) Study of thin film electrolyte with different degrees of crystalline order, from polycrystalline to single crystals, deposited by PLD.
(ii) Study of thin film electrodes with different morphologies, from dense to nanoporous.
(iii) Development of new materials for HTPC electrolytes.
(iv) Development of new cathode materials with low area specific resistance at low temperatures.
(v) Design of the micro-SOFC device and of the micromachining processing steps for its fabrication.

2. Research Activities

As a preliminary work, different SOFC electrolyte and electrode materials, and their assembly, were deposited by PLD on various types of substrates to demonstrate the feasibility of the project. Figure 1 shows an example of a multilayer structure: a Sm-doped ceria (SDC) and erbia- stabilized bismuth oxide (ESB) bilayer electrolyte was deposited on a Si (100) wafer substrate, and a cathode film made of Sr-doped lanthanum cobalto-ferrite (LSCF) perovskite-type oxide was deposited on the electrolyte top.

Fig. 1. Tri-layer of LSCF cathode, ESB, and SDC electrolyte films, deposited by PLD on (100) Si wafer.

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Nanoarchitectonics of Hybrid Artificial Photosynthetic System

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MANA Scientist Tetsuya Kako
MANA Research Associate X. Li, H. Tong, M. Amina, D. Wang
Graduate Student X. Chen, J. Cao, B. Yue

1. Outline of Research

Fundamental research and development of artificial photosynthesis technology comprising of nano-structured metal/inorganic/organic semiconductor hybrid system will be conducted. Special attention will be paid to the design of new nano semiconductor materials harvesting major part of solar light, understanding of interations between photon, carrier, molecules, and manipulation of these interations for realization of higher photon efficiency by nanoarchitectonics. A breakthrough in the efficiency of solar-chemical energy conversion is expected.

In order to accomplish this purpose, we set following four sub-themes and are conducting the materials exploration research effectively by organically coordinating these sub-themes (Fig. 1):

1) Design and fabrication of new semiconductors which can utilize solar energy sufficiently by energy band structure engineering, with the help of theorectical calculation basing on the first principle theory. Engineering of band gap as well as CB, VB potentials will be carried out simultaneously to meet the potential requirement of photosynthetic reaction.

2) Nanoarchitectonics of the photosynthesis system will be conducted, by not only fabrication of nano particles using various soft chemical method, but also assembling of nano-metal/nano-oxide hybridized system to achieve efficient transportation and separation of electron-hole charge carriers.

3) Evaluation of photon efficiency in various reactions will be performed using a solar-simulator and various gas chromatography.

4) Photosynthetic mechanism will be investigated experimentally and theoretically, to establish guidelines for development of higher efficient system.

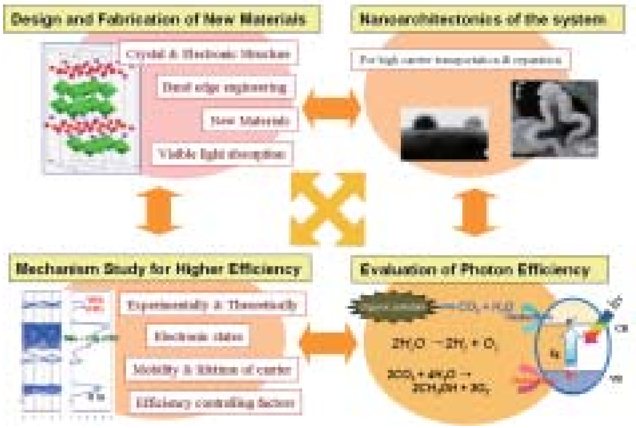

Fig.1. Four sub-themes and their organic coordination for conducting effective materials exploration research.

2. Research Activities

(1) Novel visible light active photocatalysts for efficient environment purification[1-2]*:*

A "green" chemistry process for environment purification is realized on a novel visible-light-active photocatalyst $(AgNbO_3)_{0.75}(SrTiO_3)_{0.25}$ developed by tuning band structure of $AgNbO_3$-$SrTiO_3$ solid solution. This material possesses a strong oxidative potential for efficient photocatalytic decomposition of various volatile organic compounds (VOC) (Fig. 2). A highly active photocatalyst for efficient degradation of various dyes under visible light irradiation was also successfully developed by doping nitrogen to a niobic solid acid HNb_3O_8 with unique lamellar structure[2].

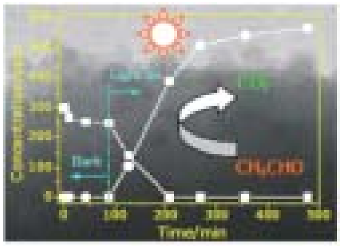

Fig. 2. Efficient decomposition of organic pollutant CH_3CHO into CO_2 under visible light irradiation over the new material.

(2) Advanced photocatalytic property explored by Nanoarchitectonics of WO_3[3]*:*

3-D hierarchical WO_3 hollow shells, including hollow dendrites, spheres and dumbbells, self-organized from tiny WO_3 nanoplatelets, were firstly synthesized by a simple soft chemical route. Distinguished visible-light-driven photocatalytic properties for organic pollutant decomposition were observed, attributed to the larger surface areas, higher crystallinity, and longer light penetration property of these unique hierarchical structures (Fig. 3).

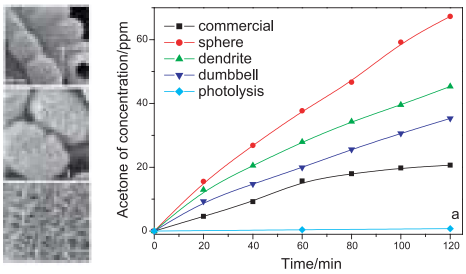

Fig. 3. Left: SEM images of the 3-D hierarchical WO_3 hollow dendrites, dumbbells and spheres. Right: Enhanced photocatalytic activity in decomposing 2-propanol into Acetone.

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Electrochemical Nanobio-sensing Devices

MANA Principal Investigator **Yuji MIYAHARA**
MANA Scientists Kohsaku Kawakami, Tetsushi Taguchi, Yoko Shirai,
Martin Pumera, Chiho Kataoka-Hamai

1. Outline of Research

Our research focuses on biomaterials and biosensors. In the biosensor projects, we are currently working on (1) the fabrication of biosensors using field-effect devices and (2) the creation of nano and micro scale materials based electrochemical biosensors, bioelectronics and biochips for ultrasensitive biosensing.

2. Research Activities

(1) Detection of supported lipid bilayers using their electric charge[1)]

The detection of electric charge in lipid bilayers was studied using field-effect devices. Large unilamellar vesicles were adsorbed onto a $Si_3N_4/SiO_2/Si$ wafer to form supported lipid bilayers (SLBs) on the solid surface through vesicle fusion. Flat-band voltage (V_{FB}) of the substrates was used to monitor the lipid's charge.

The flat-band voltage was obtained before and after SLB adsorption. We then calculated the shift (ΔV_{FB}) by subtracting the value obtained before adsorption from that obtained after adsorption. The findings of this study are that the flat-band voltage shift is dependent on the ratio of charged lipids, the salt concentration in buffers, and the surface coverage of planar bilayer patches (Fig. 1). These results demonstrate that charged bilayers can be detected from the field effect that they exert on a solid support.

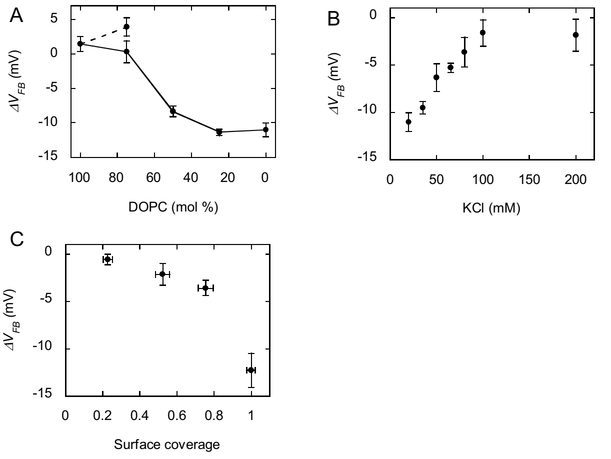

Fig. 1. Dependence of flat-band voltage shift on DOPC ratio (A), KCl concentration (B), and surface coverage (C). (A) Planar DOTAP/DOPC bilayers with full surface density (solid line) and deformed DOPS/DOPC (1:3) vesicle (dotted line). (B) Planar DOTAP bilayers with full surface coverage. (C) Planar bilayer patches of DOTAP/TRITC-DHPE (99:1) mixtures. All the experiments were performed in 10 mM potassium phosphate containing KCl. KCl concentration: 20 mM in (A) and (C). 20-200 mM in (B).

(2) Ultrasensitive hybrid nanoparticle/carbon nanotube biosensor[2)]*:*

We have developed a simple, fast and general method for facile incorporation of water-soluble metal nanoparticles in carbon nanotube/polymer composites. The gold nanoparticles/carbon nanotube/polysulfone composites were successfully prepared by the phase inversion method which involved the immobilization of nanoparticles and the soft composite coagulation at same time. The gold nanoparticles were found to be dispersed in polymer coating of carbon nanotubes. The phase inversion incorporation technique is easy, very fast (about 5 minutes for whole process) and versatile. It also allows incorporation of biomolecules to composite. The electrochemical impedance spectroscopic and voltammetric data clearly proof that gold nanoparticles enhance CNT/PSf composite and that they bring advantageous properties which should be greatly beneficial for areas of highly sensitive sensors and biosensors and for battery/energy storage applications. The phase inversion method can incorporate water-soluble metallic and semiconductor nanoparticles and quantum dots into carbon nanotube/polymer matrix in one-step process. In principle, this process is applicable for any polymer which is soluble in organic water unmixable solvent. The simplicity of the method will contribute widely to various fields of applications.[2)]

We have also contributed to understanding of electrochemistry of carbon nanotubes[3)].

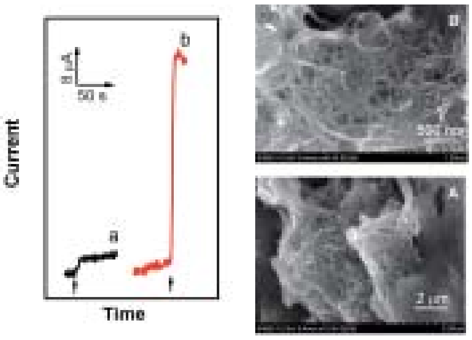

Fig. 2. left: Amperometric response of (a) HRP/CNT/PSf and (b) HRP/AuNP/CNT/PSf composite based biosensor to 2.4 mM hydrogen peroxide at potential of -0.2 V. right: Scanning electron microscopy images of gold nanoparticles/carbon nanotube/polysulfone composite at (A) 10.000× and (B) 40.000× magnification.

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Design of Stable-Radical-Containing-Nanoparticles (RNP)

MANA Principal Investigator Yukio NAGASAKI
(Satellite at Univ. Tsukuba, Japan)
MANA Scientist Kazuko Toh
Graduate Student Toru Yoshitomi

1. Outline of Research

The objective of our research is to create new biomaterials.

Because 2,2,6,6-tetramethylpiperidinyloxys (TEMPO) is susceptible for an electron paramagnetic resonance (EPR), it is anticipated as an EPR imaging probe. It also reacts with reactive oxygen species (ROS), thus, it is promising compounds as a scavenger of ROS. However, low molecular weight TEMPO is hard to utilize *in vivo* due to a preferential renal clearance and a rapid reduction. In order to improve bioavailability, we prepared stable radical-containing nanoparticles for both bioimaging probe and anti-oxidative stress drugs. We synthesized a poly(ethylene glycol)-*block*-poly(chloromethylstyrene), followed by the reaction with 4-amino-TEMPO to obtain amphiphilic block copolymer possessing stable free radicals in the hydrophobic segment (PEG-*b*-poly(PCMS-TEMPO)). This block copolymer in aqueous media forms stable polymeric micelle, which contains ca. 2,000 stable radicals in the core (stable-radical-containing-nanoparticle (RNP)).

The RNP has an interesting character that it disintegrates in response to acidic pH due to a protonation of the amino groups located in the hydrophobic core. Therefore, the RNP is expected as high-performance nanoparticle for the pH-sensitive EPR imaging probe and the anti-oxidative stress drug.

We set following themes of the RNP in this year and are conducting the exploration of an interesting performance effectively by organically coordinating these sub-themes (Fig. 1).

(i) Anti-oxidative stress drug,
(ii) *In vivo* EPR imaging probe,

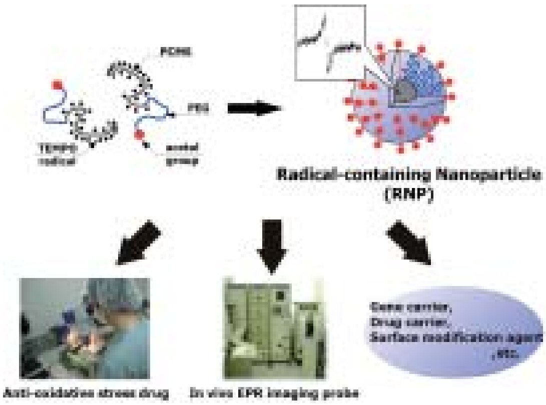

Fig.1. The themes of the RNP and their organic coordination.

2. Research Activities

(1) Synthesis of PEG-b-poly(PCMS-TEMPO) and preparation of the RNP.

Acetal-PEG-*b*-PCMS was synthesized by free radical telomerization of chloromethylstyrene (CMS) using acetal-PEG-SH as a telogen. The chloromethyl groups in the PCMS segment of the block copolymer were converted to TEMPO via an amination reaction of the block copolymer with 4-amino-TEMPO to obtain a block copolymer possessing stable radicals. The obtained block copolymer formed a core-shell type RNP in aqueous media by a dialysis method and the RNP showed pH-sensitive EPR signals as shown in Fig. 2.

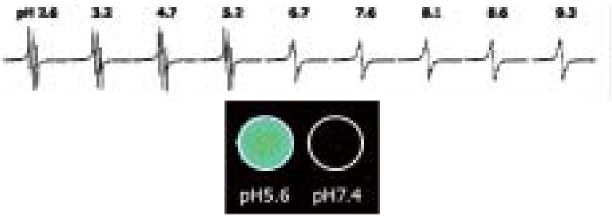

Fig. 2. EPR spectra of the RNP at various pH using X-band(upper) spectrometer and the EPR images of RNP using L-band EPR (lower) spectrometer.

(2) Evaluation as Anti-oxidative Stress Drug.

Oxidative stress causes serious damage to brain on the occasion of cerebral ischemia-reperfusion. After the reperfusion, ROS are generated, which can cause further tissue injury. The prevention of reperfusion injury is essential to minimize a degree of cerebral infarction. Our idea is to use the RNP as anti-oxidative stress drug. Because radical was compartmentalized in the core of RNP, the EPR signal of the RNP in blood stream of mice was observed even 2h after tail vein injection. It is sharp contrast against low molecular weight 4-hydroxy-TEMPO (TEMPOL), which was reduced within 2 min in blood stream. To investigate whether the RNP reduces the injured area caused by cerebral ischemia-reperfusion, the RNP was injected intravenously from a rat vein in 30 min after reperfusion (Fig.3). Consequently, the RNP significantly reduced the injury, which is promising as high performance nanoparticle for anti-oxidative stress drug.

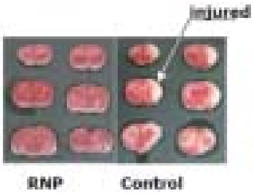

Fig. 3. The effect of the RNP on infarct volume. Coronal sections from the vehicle-treated (right) and RNP-treated rat brain (left) stained with TTC. Infarct areas were shown in white.

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Searching for New Multiferroic Materials using High-pressure Technique

MANA Independent Scientist Alexei A. BELIK

1. Outline of Research

In multiferroic systems, two or all three of (anti)ferroelectricity, (anti)ferromagnetism, and ferroelasticity are observed in the same phase. These systems may have wide technological applications because they allow control of electric properties by magnetic field and control of magnetic properties by electric field (Fig. 1). The application would include, for example, multiple-state memory elements. Multiferroic materials have been studied in the past, especially in the late 1960s in Japan and the former Soviet Union. But these studies did not attract wide attention most probably due to the lack of materials with strong magnetoelectric coupling and high ordering temperatures. Mutriferroics have experienced revival interest and return to the forefront of condensed matter and materials research in the recent years because of the advanced preparation and characterization techniques. However in the field of multiferroic materials, two major problems still remain: (1) preparation of materials with multiferroic properties at and above room temperature (RT) and (2) preparation of materials with strong coupling between different order parameters.

Materials with a perovskite-type structure are of great interest in many fields of science and technology. Their applications range from the use as catalysts or sensors to superconductors, ferromagnetic, or ferroelectric materials. A new interest appeared recently for perovskite RCrO$_3$ and RMnO$_3$ as multiferroic materials.

We aim to develop new room-temperature multiferroic materials based on the perovskite-type structure using advanced high-pressure synthetic technique. We expect to find and develop new environmentally friendly lead-free materials with ferroelectric and multiferroic properties which will have superior properties compared with the known materials. The most attractive application of these materials is in non-volatile ferroelectric random access memory (FeRAM) elements.

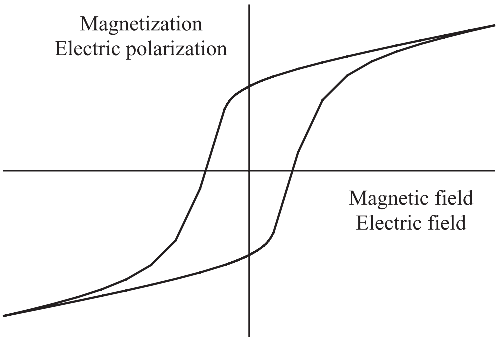

Fig. 1. **The ferroelectric and ferromagnetic hysteresis loop. It is the basis of many memory materials.**

2. Research Activities

(1) Progress in understanding the multiferroic properties of BiMnO$_3$.[1)]

We investigated high-pressure behavior of BiMnO$_3$ (Fig. 2) and also effects of the oxygen content on its magnetic and structural properties. We found that oxygen deficient BiMnO$_{3-\delta}$ samples have a non-centrosymmetric crystal structure. These findings may explain the observation of very weak ferroelectric properties in some bulk and thin film samples of BiMnO$_3$.

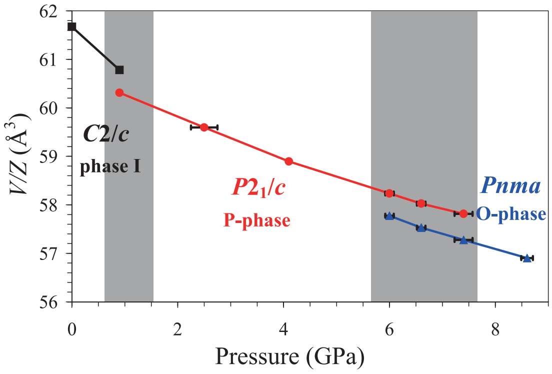

Fig. 2. **Pressure dependence of unit cell volume of BiMnO3. Two high-pressure phase transitions can be seen.**

(2) Understanding the magnetic and dielectric properties of BiCrO$_3$ and InMnO$_3$.[2)]

We investigated magnetic properties and magnetic structure of BiCrO$_3$ and found that there is nano-scale phase separation in BiCrO$_3$ into monoclinic and orthorhombic phases. We also clarified magnetic and dielectric properties of hexagonal InMnO$_3$. We showed that there is a long-range magnetic ordering in this compound and that it is a non-ferroelectric material in contrast to the previous reports.

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Next-generation Semiconductor Nanomaterials and Nanodevices

MANA Independent Scientist Naoki FUKATA

1. Outline of Research

Technical progress in silicon integrated circuits (Si VLSI) has, up to the present time, been driven by the miniaturization, or scaling, of gates, oxide layers, p-n junctions, substrates, and other elements in metal-oxide semiconductor field-effect transistors (MOSFETs), which are the building blocks of VLSI. Advances in performance and integration through conventional scaling of device geometries are, however, now reaching their practical limits in planar MOSFETs. To overcome the limiting factors in planar MOSFETs, vertical structural arrangements using silicon nanowires (SiNWs) (Fig. 1) have been suggested as the basis for next-generation semiconductor devices.

In order to realize the next-generation vertical-type MOSFETs, I will do the following subjects related to SiNWs and germanium nanowires (GeNWs), 1) size and site control with nano-scale, 2) control of surface and interface, 3) impurity doping for functionalization, 4) detection of dopant impurity, 5) passivation of defects and 6) characterization in nanoscale. In particular, it is indispensable to develop characterization methods and to investigate the site, distribution, bonding states, and electrical activity of dopant impurities in NWs. Recently, I could experimentally succeed in detecting the dopant impurities (B acceptor and P donor) and clarify their bonding and electrical states in SiNWs with diameters less than 20 nm by micro-Raman scattering and electron spin resonace methods. These results are noteworthy because these are the first experimental results for SiNWs and GeNWs. Now I stand at the forefront in area of study about the detection and the characterization of dopant impurities in SiNWs.

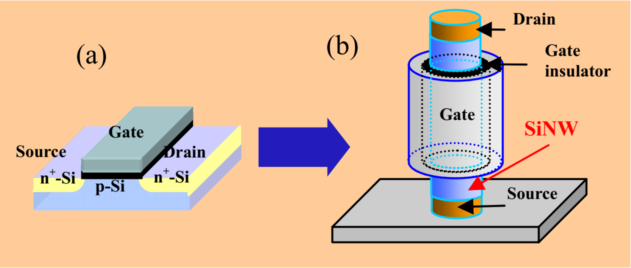

Fig. 1 Illustration of (a) planar-type and (b) vertical-type of MOSFETs.

2. Research Activities

(1) Synthesis of SiNWs

The growth of high quality semiconductor nanowires is considered to be a key point for the study of next-generation vertical-type MOSFETs. In order to achieve this point, I developed ultra high vacuum chemical vapor deposition (UHV-CVD) equipment. This special equipment made it possible to growth of defect-free SiNWs and GeNWs with uniform diameter (Fig. 2).

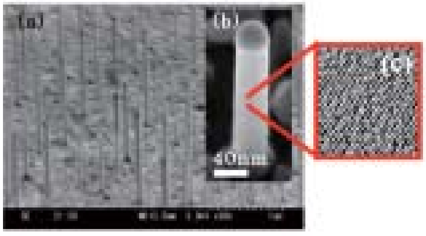

Fig. 2. (a) SEM, (b) TEM, and (c) HRTEM images of SiNWs.

(2) Doping of SiNWs[1-2)]

Micro-Raman scattering measurements were performed for undoped and B-doped SiNWs (Fig. 3 (a)). The intense peak at about 519.0 cm^{-1} is attributed to the Si optical phonon peak. This peak comes from the crystalline Si core of SiNWs. Two peaks were observed at about 618 and 640 cm^{-1} for B-doped SiNWs. These peaks were asigned to the local vibrational modes of B in SiNWs. The optical phonon peak observed for B-doped SiNWs also showed a broadening toward higher wavenumber, which is attributable to the Fano effect, showing the existence of holes.

ESR measurements were performed to further investigate the P-doping sites in SiNWs (Fig. 3 (b)). The ESR signal observed for P-doped SiNWs is deconvoluted at least to two components with g-values of 1.998 and 2.005-2.006, while no component with a g-value of 1.998 was observed for undoped SiNWs. The g-value of 1.998 corresponds to that of conduction electrons in Si, indicating that the ESR signal can be attributed to the conduction electrons in the Si core of the SiNWs. This result proves that P atoms were clearly doped in substitutional sites of the crystalline Si core of SiNWs, resulting in the formation of n-type P-doped SiNWs.

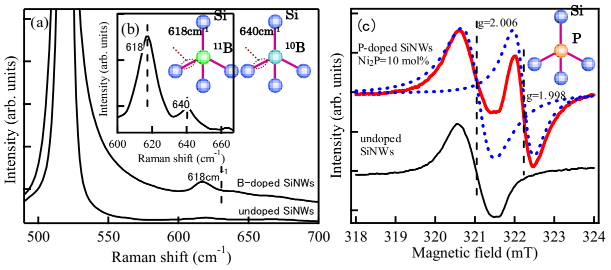

Fig. 3. (a) Raman spectra observed for B-doped SiNWs and undoped SiNWs. (b) The magnification of (a). (c) ESR signals observed for P-doped SiNWs and undoped SiNWs.

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Organic-Metallic Hybrid Polymers: Synthesis and Electrochromic Properties

MANA Independent Scientist Masayoshi HIGUCHI

1. Outline of Research

I aim to fabricate organic-metallic hybrid polymers consisting of coordination bonds and make clear their structure by using an atomic-force microscope and others. I hope to discover their excellent electrochromic properties based on electrochemical control of the metal-to-ligand charge-transfer (MLCT) absorption, and succeed in applying it to solid-state devices. A series of results suggest a possibility of applying the hybrid polymers to energy-saving devices such as color electronic paper.

Electronic paper is drawing attention as one of next generation display devices to follow the liquid crystal, plasma, and organic electro-luminescence (EL) displays. Unlike the present display devices, the display continues after the power is cut. Therefore, it is expected to play the role of paper media for newspapers and others in the future, as a resource and energy saving display device. Up to now various methods are proposed as the display mechanism for electronic paper including the micro capsule method. However, most of them are monochromatic (black and white) display and realizing color display is the task to be achieved.

As a scheme suitable for color display, electrochromic display (a display method using an electrochromic material which changes color through the electrochemical oxidation-reduction process) is known, but only a small amount of research is being pursued compared with other methods. The reason is twofold: one is due to its own proper drawbacks (material's low durability, slow response, difficulty in making solid-state devices), and the other is due to extremely strong dependence on the material's superiority or inferiority of this method's value. To put it the other way around, if the material is developed that is suitable for the application to electronic paper, it is possible that this method could become the breakthrough of color electronic paper.

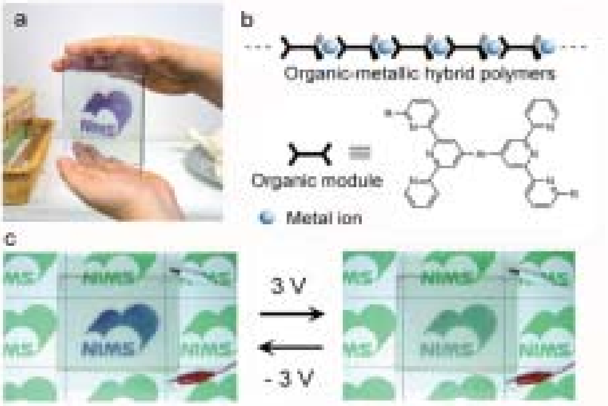

Fig. 1. Organic-metallic hybrid polymer having electrochroimic Properties.

2. Research Activities

(1) Synthesis of organic-metallic hybrid polymer:

We developed organic-metallic hybrid polymers (Fig. 1b). These polymers are formed by self-assembly of metallic ions and organic compounds which have two sites having strong coordination toward metallic ions (organic modules). They develop color through absorption based on charge transfer from metallic ions to the organic modules (MLCT). We discovered the phenomenon of color disappearance on the polymer according to the applied electric potential (electrochromic phenomenon), when we cast this polymer onto ITO glass and electrochemically caused oxidation-reduction. This transition between color development and color disappearance occurs at the threshold voltage corresponding to the oxidation-reduction potential of the metal in the polymer.

(2) Fabrication of electrochromic display devices using this polymer:

By spin-coating ITO glass with the polymer and covering it with a layer of gel electrolyte and another sheet of ITO glass, we fabricated the device 5 inches in dimension as shown in Fig.1a. By applying an electric potential (3V) with two dry batteries, we could repeat alternately development and disappearance of color (Fig.1c). Hybrid polymers can develop various colors with different combinations of organic modules and metallic ions (Fig. 2). We also confirmed their stability by repeating the color development 4,000 times; they have higher stability than usual organic electrochromic materials.

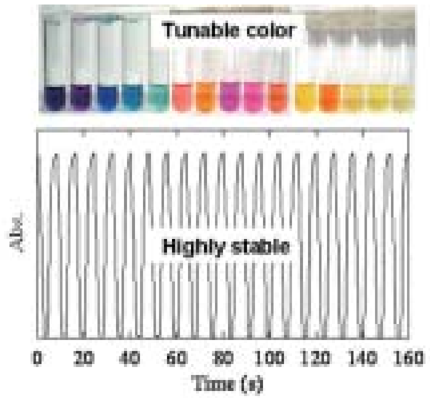

Fig. 2. Multi-color display with hybrid polymers.

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Graphene-based Quantum Devices

MANA Independent Scientist Satoshi MORIYAMA

1. Outline of Research

Graphene, single atomic-layer of graphite, is one of the attractive two-dimensional conducting materials for building blocks of novel quantum electronics. The recent discovery of single- and few-layer graphene has opened a door to a new area of low-dimensional physics. 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 few-layer graphene make it possible candidate for future nano-electronic devices.

Our research objective is the realization of quantum wires and quantum dots in graphene-based materials by using the nano-fabrication process, toward the novel graphene-based quantum devices. It will be expected that the fabricated quantum wires or quantum dots become integrated quantum circuits because of its 2-dimensional sheet structure. Furthermore, their low atomic weight and the low nuclear spin concentration, arising from the only 1.1% natural abundance of ^{13}C are expected for having weak spin-orbit interactions and hyperfine interactions. Therefore, graphene-based quantum devices are promising candidates for spin-based quantum information processing and spintronic devices.

2. Research Activities

(1) *Spatially resolved Raman Spectroscopy in graphene and graphene layers*[1)]

The ability to dope carriers is crucial for future application and the Raman spectroscopy is a sensitive probe of the doping with a spatial resolution. Actually, gate-modulated low-temperature Raman spectra was measured and it was revealed that the electric field effect leads to doping and has a large influence on the phonon structure of graphene and Raman spectra. Since it can be a basis field-effect-transistor structure, it is promising that the Raman spectroscopy plays an important role in the characterization of graphene nano-devices. As an initial stage of this development, we systematically investigated spatially resolved Raman spectroscopy measurements on single- and few-layer graphene flakes, varying the excitation wavelength. Figure 1(a) shows an optical microscope image of graphene flakes on 300 nm thick SiO_2. Optical microscope contrast can be identified the single-, double- and triple-layer graphene. Figure 1(b) shows the Raman mapping of the integrated *G*-band Raman peak in the dashed square region in Fig. 1(a). The intensity of *G*-band peak is also reflected the number of layers among single- double–and triple-layer graphene.

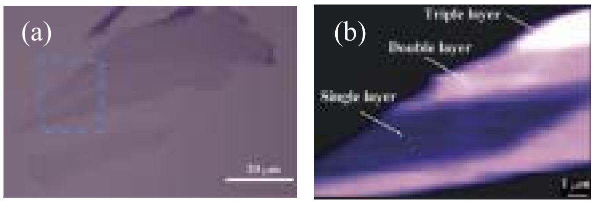

Figure 1. (a) Optical microscope image of graphene flakes on SiO_2/Si. (b) Raman mapping of the integrated intensity of *G*-band Raman peak in the dashed square region in (a).

The spatially resolved Raman spectroscopy also reveals the phonon dispersion of single- and few-layer graphene based on not only *2D*-band but also *D*-band which can be assigned translational symmetry breaking or to defects and is only observed at the section boundaries between graphene and substrates.

(2) Fabrication of graphene-based quantum dot devices

After characterization of graphene flakes by Raman spectroscopy, we proceed to make the contact to the graphene, and patterning. Graphene nanostructures can be fabricated by carving out of the graphene sheet. It has the possibility of the realization of graphene nano-devices such as quantum wires and quantum dots. Figure 2 shows one of our working graphene-based 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 $S \approx 0.005\ \mu m^2$), and the constrictions were equal length and width of about 15 nm. We demonstrate a graphene-based double quantum-dot system for the first time, 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 nanoelectronics.

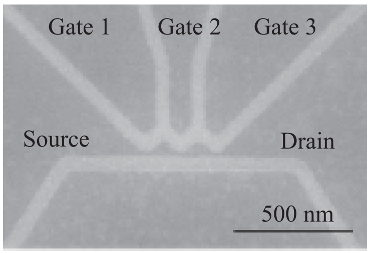

Figure 2. Scanning electron microscope image of our fabricated device with electrode assignment.

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Atom-scale and Mesoscale Infrared Plasmons

MANA Independent Scientist Tadaaki NAGAO

1. Outline of Research

Interface and size/shape effects often serve as the vital secret for tailoring the functional properties of nanoscale materials. We have been working on revealing such effects as Rashba spin orbit coupling effect [1)] and the surface enhanced infrared absorption [2)] of nanoscale metallic materials. In metallic materials, electrons oscillate in a collective manner with ultrahigh frequencies. This oscillation is called plasmon and shows strong shape and dimensionality effect when they are confined in nano-scale tiny objects. Thanks to this remarkable properties the world-wide active research field has emerged recently that aims at controlling the propagation, scattering, and the polarization of light in nanometer scale. Normally, the plasmon frequency lies in visible to ultraviolet regime, but when the object size becomes atomically thin [3)], and the interaction between the objects becomes significant, the oscillation frequency shifts down to the infrared regime with tiny nano-scale propagation wavelength.

In this project, we will establish the way for applying this novel knowledge for the realization of new classes of optical materials. We will explore various nano-metallic architecture, by adopting nanofabrication, colloidal process, as well as molecular beam atomic-layer epitaxy. In this way, we will establish a new methodology for realizing innovative infrared optical materials.

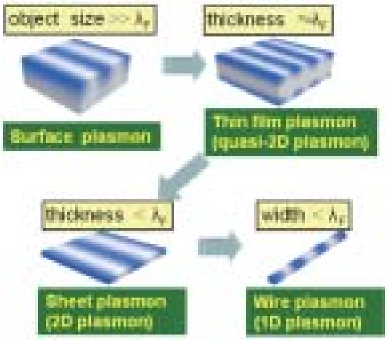

Fig. 1. Size and dimensionality effects on plasmons of metallic nano-materials. λ_F is the Fermi wavelength of the materials.

2. Research Activities

(1) Plasmons in atom sheets and atom chains

We have fabricated some metallic chain structures on silicon substrates and measured the confined plasmons by use of low-energy electron spectroscopy with high momentum resolution. For the case of 1nm-wide In chains, we clarified that plasmon extinguishes and reappears at the metal-to-insulator transition (MIT) of the chains due to Peierls instability [4)]. We also measured an infrared plasmon in Au-Si atom chains and proposed that the plasmon arises from the Si graphitic chains of this system. The infrared spectroscopy was performed for In atoms chains and we detected the MIT behavior also in the optical spectroscopy.

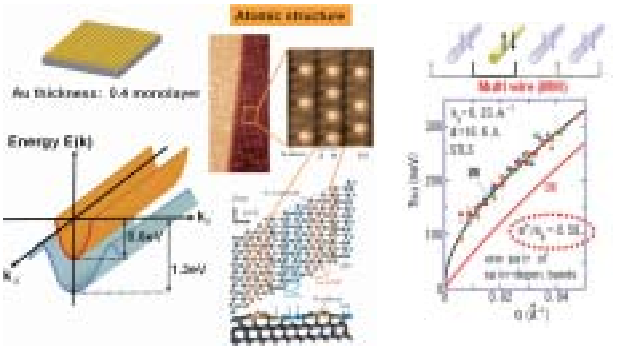

Fig. 2. Atom chains of Au-Si complex chains and Si graphitic chains supported on Si substrate.

(2) Plasmon enhanced vibrational spectroscopy

We have developed a new methodology in tuning the gap width, filling factor, and the number of the hot spots of the Au tabular islands for the infrared antenna resonance for chemo/bio sensor materials [5)]. The infrared beam itself was used to determine the enhancement in the absorption of molecular signal as well as the infrared plasmon resonace so that we can judge the infrared activity in situ to optimize film growth condition in aqueous solution. The vibrational signal as high as 15-20 % was routinely obtained from adsorbed organic monolayers such as octadecanethiol (ODT), dithiocarbamate (DTC) etc.

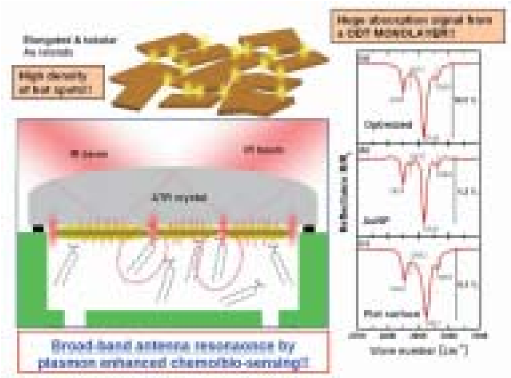

Fig. 3. Structure optimized Au tabular islands for infrared antenna resonance with very high surface enhanced infrared activity.

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Development of Photoresponsive Biointerfaces

MANA Independent Scientist Jun NAKANISHI

1. Outline of Research

Biointerfaces are interfaces between biomolecules and materials. They play pivotal roles in biomedical devices such as materials for drug delivery, tissue engineering, and biosensing. Therefore, it is important to understand and engineer the biointerfaces for such advanced applications. The purpose of the present study is to develop novel functionalized biointerfaces by the chemical modification of material surfaces with photochemically active compounds and apply them for controlling cellular functions as well as for engineering tissue mimics *in vitro* (Fig. 1).

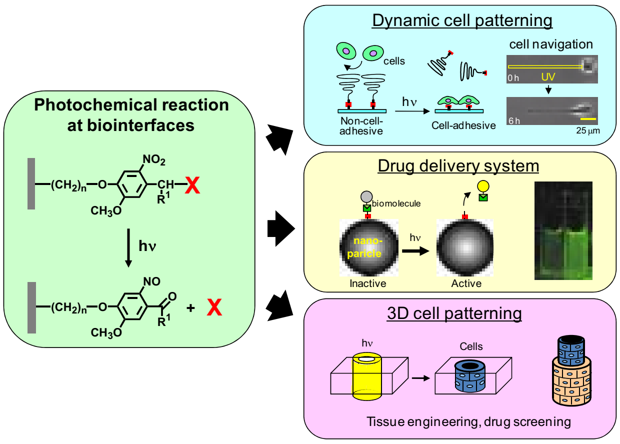

Fig. 1. Photoresponsive biointerfaces developing in this study.

2. Research Activities

(1) Photoactivatable cell culture substrate.

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. To fill the gap between them, we have developed several photoactivatable cell culture substrates.[1,2] One of which is a glass coverslip grafted with a photocleavable poly(ethylene glycol) (PEG). The substrate changed from non-cell-adhesive to cell-adhesive by the photocleavage of PEG. Cellular patterns maintained for more than 17 days, and they were able to be changed by irradiating their adjacent regions during cell cultivation. By taking advantage of this feature, we succeeded in selective proliferation of a single cell clone by controlling irradiating regions (Fig. 2). This technology will be useful for cloning valuable cell populations from a heterotypic cell mixture.

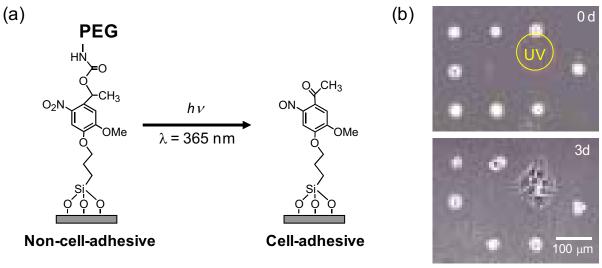

Fig. 2. Photoactivatable cell culture substrate based on photocleavable PEG. (a) Scheme. (b) Selective proliferation of a single cell clone.

(2) Photoresponsive nanocarrier[3]*.*

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 (Fig. 3). 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. The present approach will be useful to deliver other amine derivatives such as neurotransmitters, peptides and inhibitors. Furthermore, since GNPs are easy to add chemical functionalities through thiol linkage, we will be able to deliver the GNPs inside living cells by introducing membrane-translocating peptides such as an arginine-rich peptide. This modification further opens up the new possibilities of direct regulation of intracellular signaling networks.

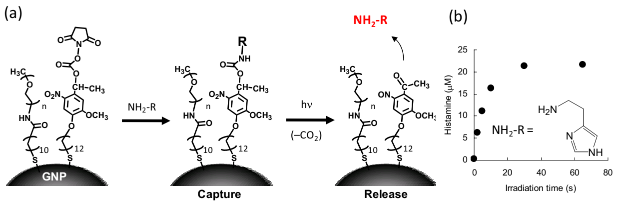

Fig. 3. Photoresponsive delivery system for amines based on the GNPs having a photocleavable succinimidyl ester. (a) Scheme. (b) Dose-dependent histamine release from the GNPs.

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Computational Physical Chemistry

MANA Independent Scientist **Yoshitaka TATEYAMA**

1. Outline of Research

We are challenging to make novel theoretical frameworks for phenomena in physical chemistry such as electron transfer, proton transfer & photoexcitation, since these processes play crucial roles in energy & environmental issues, while computational methods for them are less established than the conventional techniques for ground state properties.

Our main projects are as follows; (1) development and/or establishment of theories and computational methods for problems in physical chemistry based on the "density functional theory (DFT) and ab-initio calculation techniques", (2) understanding microscopic mechanisms of elementary reactions in physical chemistry problems by applying these DFT-based and ab-initio techniques. The particular fields of targets are electrochemistry, photochemistry, solution chemistry, interface chemistry, proton and defect science.

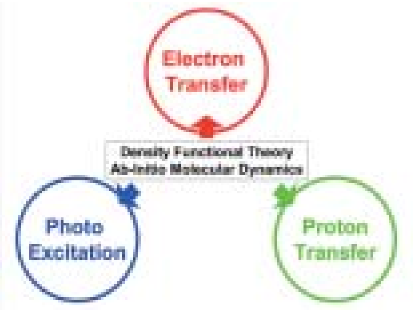

Fig.1. Research targets in our computational physical chemistry team.

2. Research Activities

(1) Calculation of electronic excitation spectra by Time-Dependent DFT (TDDFT) Conventional & Modified Linear Response (LR) schemes

Accurate prediction of absortption spectra is still a big challenge of ab initio DFT calculation. We have explored validity and limitation of the computational methods based on the TDDFT-LR scheme developed for excitation energy calculation. In a calculation of valence excitation in a transition metal complex, we found an anomalous behaviour that TDDFT-LR gives a large overestimation of excitation energy contrary to typical underestimation.[1] This suggests that we need to reconsider the physical meaning of the interactions and orbitals involved in the scheme. Modified LR scheme was proposed to remedy the drawback of TDDFT-LR that charge transfer and Rydberg excitation energies are significantly underestimated. We examined the validity of this TDDFT-MLR scheme for atomic systems that have many types of Rydberg excitations, and demonstrated that the TDDFT-MLR scheme can work well in those systems as well.[2] In this work we also presented what initial states should be taken for spin-specified excitations.

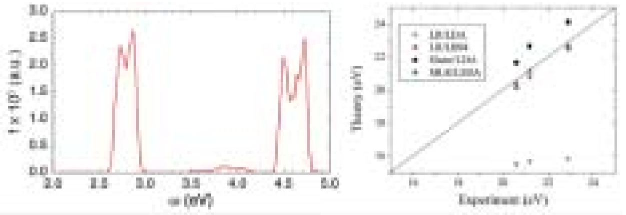

Fig. 2. Excitation spectra/energies of hydrated transition metal complex by TDDFT-LR (left) and helium atoms by TDDFT-MLR (right).

(2) Ab Initio Molecular Dynamics Study on Redox reactions in Electrolyte Solution

We have recently established ab initio molecular dynamics (MD) methods for redox reactions: DF-MD or DF-Constrained MD -Energy Gap methods, which can deal with any types of redox reactions involving bond breaking/formation as well as electron transfer.[3]

For further validation of those methods, we have applied them to triiodide redox reactions in solution, which involve multiple electron transfer and bond change. These iodide electrolyte solutions have been frequently used, while the atomistic mechanisms haven't been fully understood. Our calculations of redox potentials of the intermediate processes imply that triiodide dissociation initially occur in water, while the reduction is more probable in MeCN solution. We then proposed that higher efficiency in the latter solution is attributed to the priority of electron transfer.

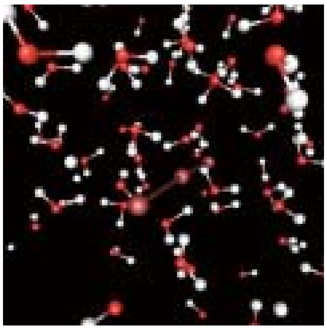

Fig. 3. Snapshot of triiodide in aqueous solution.

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Superconductivity of FeSe and Related Compounds

MANA Independent Scientist Shunsuke TSUDA

1. Outline of Research

The purpose of this study is clarification of iron-based superconductivity. The highest superconducting temperature (T_c) is above 55 K. This is surely higher temperature than the temperature expected by the conventional theory of superconductivity. Actually, the iron-based superconductors show much evidence of unconventional superconducting features.

Similarly to copper oxides superconductors, iron-based superconductors can be categorized into 4 groups in the structure. We listed them in Fig. 1. The common feature is square lattice of iron layer. While the superconducting mechanism is not clarified, it is widely accepted that the iron layer is essential key. Here we focused on FeSe and it related compounds as in the Fig. 1 (c). Those have the simplest structure among iron-based superconductors. Therefore, these compounds may give us a chance to understand the superconducting mechanism.

In this study, we studied FeSe and its related compounds by applying artificial perturbation, such as pressure and chemical substitution.

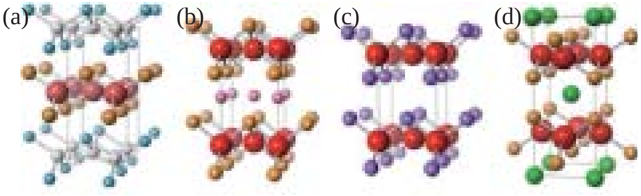

Fig. 1. The crystal structures of the iron based superconductors. (a) 1111 structure (b) 111 structure (c) 11 structure (d) 122 structure. (http://www.jst.go.jp/extra/2008/081031.html)

2. Research Activities

(1) Superconducting Properties and its pressure effect of the Iron-based superconductor FeSe[1)]

We synthesized polycrystalline FeSe and its related materials. The temperature dependence of resistivity and the temperature dependence of magnetization clearly show superconductivity. One of the outstanding features of FeSe is external pressure effect. Figure 2 shows pressure dependence of the T_c. The pressure enhanced superconductivity. Especially the superconducting onset temperature was pushed up more than twice. LaFeAsO shows enhancement of T_c by external pressure and substitution of La by other rare earth enhanced T_c. Therefore current result may indicate that appropriate substitution may realize higher T_c in this 11 system.

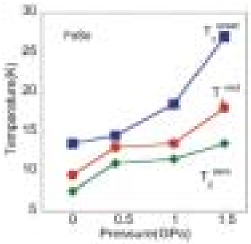

Fig. 2. Pressure dependence of T_c for FeSe [1)]**.**

(2) Substitution effect of FeSe[2,3)]

We performed systematic substitution study for the Se site by S and Te. This substitution does not affect on the band filling. However, as is shown in the fig. 3, the T_c strongly depends on the substitution. These facts suggest that carrier doping is not essential in contrast to $LaFeAsO_{1-x}$. On the other hand, Fermi surface nesting may induce magnetic ordering. The substitution of S and Te for Se in FeSe modifies band structure and Fermi surface topology. Therefore the band modification should affect on the magnetic order and/or superconductivity. This result reinforces this story.

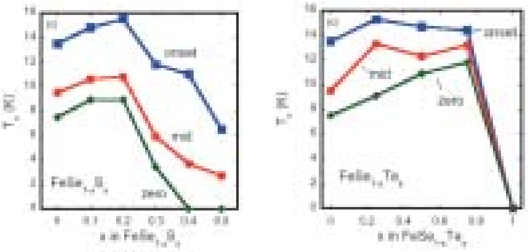

Fig. 3. S and Te substitution dependence of T_c for FeSe[3)]**.**

(3) Photoemission study of FeSe[4,5)]

We performed high-resolution photoemission study on FeSe and $FeSe_{1-x}Te_x$. Similar to 1111 compounds, we observed pseudo gap like feature around the Fermi level. The origin of the pseudo gap is not clarified yet.

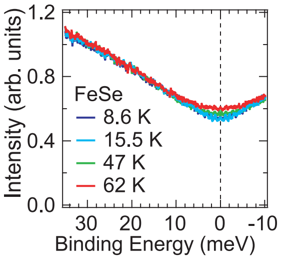

Fig. 4. Symmetrized photoemission spectuectra for FeSe.

These studies were corroboration with Y. Mizuguchi, Y. Takano in NIMS, S. Shin and his coworkers in ISSP, Univ. of Tokyo, T. Yokoya and his coworkers in Okayama Univ.

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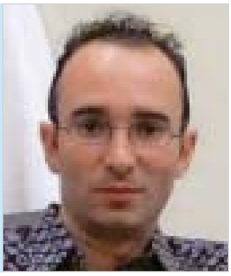
Metal Oxide Semiconductor Nanorod-based Structures & Devices

MANA Independent Scientist Lionel VAYSSIERES



1. Outline of Research

We aim to contribute to the development of a new generation of materials using nanoscale and quantum confinement phenomena to create multi-functional structures and devices for energy, electronics, & medicine by cost-effective large scale fabrication techniques[1]. For instance, we are developing novel key semiconductor materials for solar hydrogen generation, photovoltaics, and sensing applications.

In order to accomplish the challenging goals, we are utilizing low cost materials chemistry techniques such as aqueous chemical growth and plasma enhanced chemical vapor deposition and their combination to fabricate visible light active semiconductors based on quantum-confined metal oxide nanostructures and devices.

We set the following two type of material development approaches based on quantum confinement effects such as quantum dot multi-excitonic effect and intermediate band effects (Fig.1) to fabricate novel semiconductor structures and devices for low temperature chemical and gas sensor applications[2] as well as visible light-active semiconductors for solar hydrogen generation and photovoltaics.

(i) Doped and undoped metal oxide vertically oriented nanorod arrays fabricated by low temperature chemical and gas phase techniques onto various transparent conducting oxide substrates;

(ii) Quantum dots sensitized quantum rods metal oxide vertically oriented arrays fabricated by low temperature aqueous chemical growth onto various transparent conducting oxide substrates.

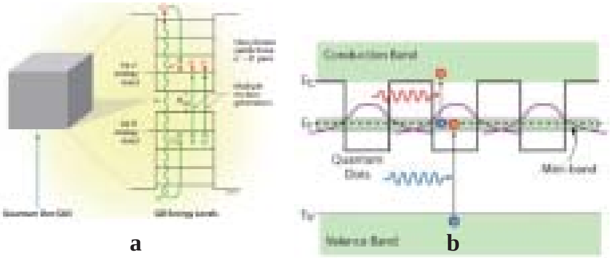


Fig. 1. Scheme of the mechanisms of (a) multi-excitonic generation and (b) the intermediate band effect in quantum dots.

2. Research Activities

The modeling, synthesis, and in-depth synchrotron radiation-based electronic structure characterization of nanorod-based transition metal oxide nanostructures and devices are being carried out at NIMS and at Lawrence Berkeley National Laboratory. After the pioneering development of vertically oriented nanorod-arrays of α-Fe_2O_3, ZnO, and SnO_2 at low temperature by aqueous chemical growth for photovoltaic and gas sensors[2], our recent focus has been on doped- and hetero-nanostructures for visible light active semiconductors[3].

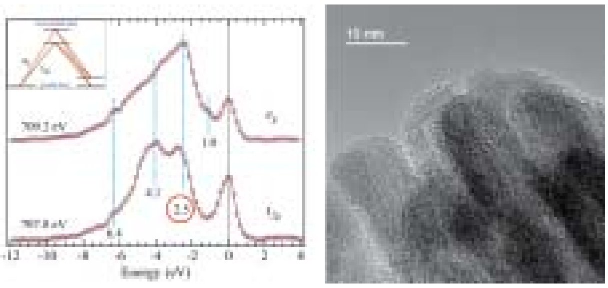


Fig. 2. Synchrotron-based resonant inelastic x-ray scattering spectra of hematite vertically oriented quantum rod-arrays showing 1-D bandgap confinement effect.

We have synthesized and characterized the electronic structure (Fig.2) and basic structural, optical, and photoelectrochemical properties of novel visible light active iron oxide-based semiconductors consisting of vertically oriented arrays of doped iron oxide as well as quantum dots sensitized quantum rods iron oxide (Fig.3) showing extended visible light absorption, fast interfacial kinetics, low bias operation at neutral pH environment which enable the use of seawater as unique electrolyte for efficient and low cost water splitting.

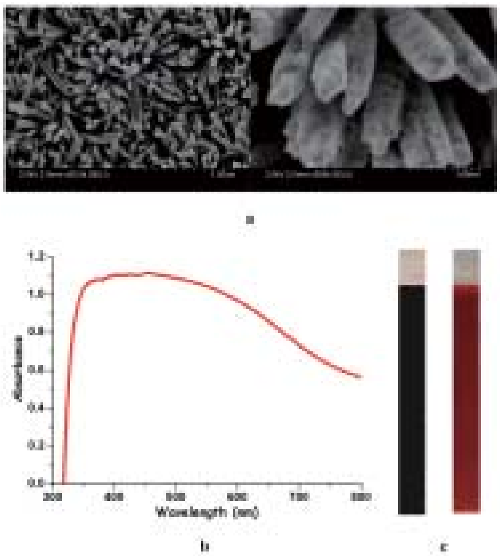


Fig. 3. (a) SEM images of vertically oriented arrays of quantum-rod sensitized quantum-dot iron oxide-based hetero-nanostructures; (b) UV-Vis absorption spectrum of novel nanostructures showing full visible light absorption profile; (c) Still image of doped (black) and undoped (red) iron oxide photo-anodes.

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Nanoporous Nitrides and Metallosilicates and their Catalytic Functions

MANA Independent Scientist Ajayan VINU

1. Outline of Research

Since the discovery of mesoporous silica molecular sieves designated as M41S, this field of research has been tremendously focussed and considerable scientific effort has been involved on the preparation, characterization and application of novel class of ordered mesoporous materials. These ordered mesoporous materials exhibit very high specific surface area, specific pore volume, tunable pore size and controllable morphology. These excellent textural characteristics of the mesoporous materials enable them to function as promising candidates for a large spectrum of applications including size and shape selective adsorption, chromatographic separation, multifunctional catalysis, nanoreactors, immobilization of biomolecules, and biomedical engineering. However, the neutral charge and low acidity and stability of the mesoporous silica materials do not support their application in the field of catalysis.

Our aim is to fabricate the materials which can be utilized for either acidic or basic catalysis. Firstly we propose to fabricate the materials which are composed of nitrogen and other elements such as carbon and boron and these materials promise access to even-wider range of application possibilities because of their unique properties such as semi-conductivity, intercalation ability, hardness, and basicity. Secondly, we aim to fabricate materials with the metallosilicate framework with tri or penta valent metals.

Carbon nitride (CN) is a well known and fascinating material that has attracted worldwide attention because the incorporation of nitrogen atoms in the carbon nanostructure can enhance the mechanical, conducting, field emission, and energy storage properties. Owing to its unique properties such as semi-conductivity, intercalation ability, hardness, CN is regarded as a promising material which could find potential applications in many fields. CN materials with no porous structure can be prepared either from molecular or chemical precursors at very high temperatures.

2. Research Activities

(1) *Discovery of mesoporous carbon nitrides with tunable pore diameters, surface area, and nitrogen contents*[1)]

Here, we report for the first time on the preparation of hexagonally ordered mesoporous carbon nitride (MCN) materials with tunable pore diameters, surface area, pore volume and nitrogen content through the polymerization reaction between ethylenediamine (EDA) and carbon tetrachloride (CTC) using SBA-15 with various pore diameters as template (scheme 1). The pore diameter of the above materials has been tuned by changing the pore diameter of mesoporous silica template with keeping the weight ratio of carbon and nitrogen source constant. The textural parameters and the nitrogen content of the MCN materials can also be controlled by the simple adjustment of the weight ratio of the carbon to nitrogen source in the synthesis mixture. Finally, the catalytic activity of the MCN-1 materials with different pore diameters was tested in the Friedel-Crafts acylation of benzene using hexanoyl chloride as the acylation agent and heptane as the solvent. Among the catalysts studied, MCN-1 with the highest nitrogen content and surface area shows the highest conversion and 100% product selectivity to caprophenone.

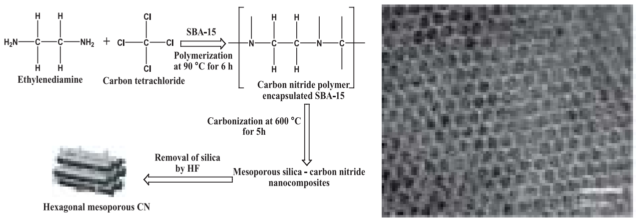

Fig. 1. Preparation of Nanoporous CN using SBA-15 template. Right: HRTEM image of MCN.

(2) *Discovery of Nanoporous Three Dimensional Aluminosilicate Nanocage,*[2,3)]

Here, we strikingly demonstrate a facile direct synthesis route for the preparation of 3D-aluminosilicate nanocage materials with extremely high loading of Al, up to the n_{Si}/n_{Al} ratio of 10 by the simple adjustment of the molar water to hydrochloric acid ($nH_2O/nHCl$) ratio of the synthesis gel via templating with a Pluronic F127 in a highly acidic medium. The pore diameter of the materials can simply be controlled by adjusting the incorporation of Al atom in the silica framework. Interestingly, it was found that the pore diameter, unit cell constant, and the pore volume of the materials increase with increasing the loading of Al in the silica framework. Finally, the activity of the catalyst in the acetylation of veratrole by acetic anhydride has been tested, which is much higher than the zeolite and zeotype materials.

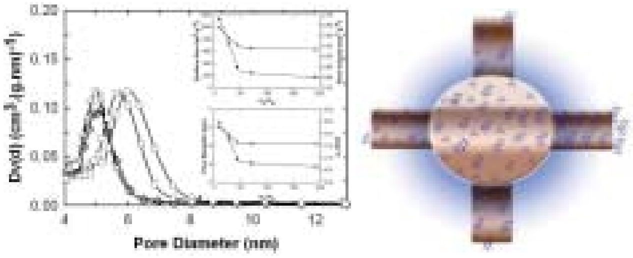

Fig. 3. BJH adsorption pore size distributions of nanoporous 3D-aluminosilicate nanocages prepared at different n_{Si}/n_{Al} ratios: (◇)193, (▽) 71 (△) 44, (□) 28, and (○) 10 (insets: the effect of nSi/nAl ratios on the textural parameters of the samples. Right: Catalytic reaction pathway over the nanocage.

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Design of Nanoarchitectured Metals: New Insight into Mesoporous Materials

MANA Independent Scientist Yusuke YAMAUCHI

1. Outline of Research

Because of their scientific and practical significance, research on mesoporous materials, conducted mainly by using surfactant assemblies as templates, has been increasing rapidly. The specific features of regular pore arrangement, uniform mesopore size, and high surface area make these materials very promising for various applications. Mesoporous metals with high electroconductivity have attracted particular interest for their very wide range of applications in such items as batteries, fuel cells, solar cells, chemical sensors, field emitters, and photonic devices. Although several mesoporous metals have been prepared in the past, the mesostructures of these metals are less ordered than those reported for inorganic oxides such as silica.

Therefore, the rational design of highly ordered mesoporous metals with controlled compositions and morphologies for practical applications is a most attractive and challenging objective. My MANA research interest is evolution and practical application of new types of mesoporous metals, especially mesoporous alloys and films with oriented mesochannels.

2. Research Activities

(1) Mesoporous Pt rods[1]

We newly proposed a generic platform for the preparation of new types of Pt fibers having stacked donut-like mesostructures with an excellent arrangement of uniformly sized nanoparticles. Here, we clearly demonstrate that the collaboration of both LLC (lyotropic liquid crystals) templating by electrochemical processes and hard templating utilizing a confined effect can lead to the genesis of new nanostructured metals. Such a unique metal-based nanoarchitecture enhances the surface area and enables the high-mass transportation of guest species. Preferentially oriented mesochannels should contribute significantly to the fine control and transport of electronic carriers through metal fibers.

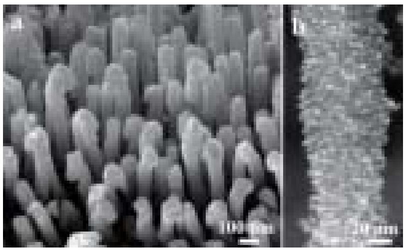

Figure 1. SEM images of mesoporous Pt rods.

(2) New mesoporous metals with giant mesopores[1]

To further explore the potential properties of nanoarchitectured metals, the versatile control of mesostructures and pore size is vital. We demonstrated the preparation of a new type of mesoporous Pt particle with giant mesocages connected closely in three dimensions, templated from LLCs consisting of diblock copolymers. The size of the mesocages is the largest (about 15 nm) reported in mesoporous metals. The advantage of diblock copolymers is that their high molecular weight and composition are well designed. By utilizing LLCs made of such designed block copolymers, new nanoarchitectured metals with various mesostructures and pore sizes should be realized. Giant mesopores can incorporate large biological molecules, and also volume changes caused by incorporation of guest species into host matrices are effectively relaxed. Cage-type mesostructures should enhance the accessibility of various species.

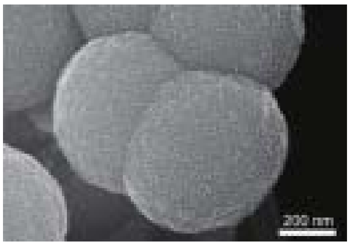

Figure 2. SEM image of giant mesopores.

(3) Orientation controls of mesochannels[2]

We report the formation of standing mesochannels simply by spin-coating a precursor solution onto a PAA (porous anodic alumina) substrate with designed conical holes, utilizing exactly the same precursors and reaction conditions that form two-dimensional (2D) hexagonal mesoporous SBA-15-type films. When the aspect ratios of the conical holes are lower, the sponge-like mesopores are generated within the conical holes. Such a formation of sponge-like mesostructures truly acts as a trigger for the evolution of perpendicularly oriented and tilted mesochannels. On the other hand, when the PAA substrates with high-aspect cones are used, the mesochannels are stacked like a doughnut within the conical holes, which leads to parallel orientations of the mesochannels in the continuous film region. Our new class of films represents a significant breakthrough in mesoporous materials science and could lead to a vast range of applications, such as highly sensitive chemical sensors, highly selective separation, and ultrahigh-density magnetic recording media.

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A Novel Biointerface with Well-defined Well-controlled “Concentrated” Polymer Brushes

MANA Independent Scientist Chiaki YOSHIKAWA

1. Outline of Research

Recently living radical polymerization (LRP) has been successfully applied to graft polymerization and grafted well-defined polymers on inorganic/organic substrates with an extremely high graft density. Such densely grafted polymers have been classified into the “concentrated” polymer brush, giving characteristic structure and properties$^{1)}$: for example, in a good solvent, these brushes are highly extended, nearly to their full length, providing strong resistance against compression, ultra-low friction (or super lubrication), and size exclusion with a limit set for a very low molecular weight (Fig. 1). Focusing on the unique structure and properties of the concentrated brushes, I 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.

In order to accomplish this goal, I plan to elucidate the mechanism of interactions between concentrated brushes and biomolecules such as protein and cell.

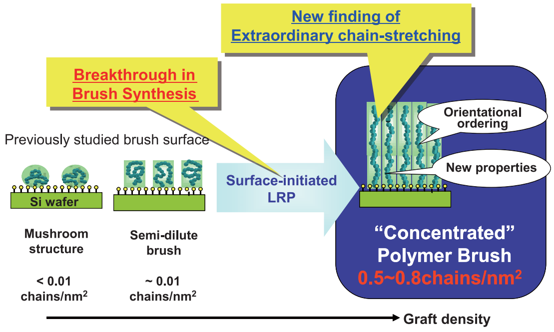

Figure 1. Development of concentrated polymer brush.

2. Research Activities

1) HUVEC and Platelet Adhesions on “Concentrated” Poly(2-hydroxyethyl methacrylate) Brush.$^{2)}$

Recently I reported that the concentrated poly(2-hydroxyethyl methacrylate) (PHEMA) brush suppressed protein adsorption compared to the semi-dilute brush because of its unique size-exclusion effect.$^{3)}$ Since protein non-specific adsorptions often trigger cell adhesions, the concentrated PHEMA brush would be expected to suppress cell adhesions. In this work, I examined HUVEC and platelet adhesions. PHEMA is often used for coating of inner surface of an artificial blood vessel. As I expected, concentrated PHEMA brush suppressed HUVEC and platelet adhesions compared to the semi-dilute brush (Fig. 2). These results indicate that PHEMA concentrated brush would be excellent blood compatible surfaces.

Figure 2. The fluorescence micrographs of HUVEC adhered onto (a) semi-dilute PHEMA brush and (b) and (c) concentrated PHEMA brush with different graft thicknesses. HUVEC incubated for 24 h.

2) Proteins Adsorption and Cell Adhesion on Concentrated Polymer Brushes: Effect of Polymers.

In order to control interaction of polymer brush with protein and cell, the chemical composition of the brush is also an important factor. Thus I examined protein and cell adhesions on concentrated polymer brushes with different polymers. In this work, I examined three neutral hydrophilic polymers, PHEMA, poly(2-hydorxyehtyl acrylate) (PHEA), and poly(poly(ethylene glycol) methyl ether methacrylate) (PPEGMA). Interestingly, those concentrated brushes similarly suppressed protein and cell adhesions, even though contact angles, i.e., surface energies of those brushes were different (Fig.3). The details are now investigating.

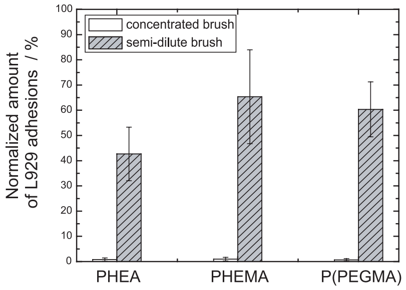

Figure 3. Amount of adhered L929 cells on PHEA, PHEMA, P(PEGMA) brushes with different graft densities. Cells were incubated for 24 h. Dry thickness was 2 nm.

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Multidimensional Atomic Scale Semiconductors

ICYS-MANA Researcher Somobrata ACHARYA

1. Outline of Research

The prime motivation of nanotechnology is to reach atomic scale dimensions and increase integrity of devices with enhanced performance at atomic scale. However, the major obstacle has remained in developing materials with ultra-narrow dimension below the Bohr radius (in the very strong confinement regime) with superior control over their size and shape distribution. In addition, application limit is now struggling due to working limitations of the existing lithographic techniques and hundreds of leading groups in the world are working on this challenge. We are consistently preparing multidimensional nanomaterials below the Bohr radius with superior control over their distribution far below lithographic limit. We came up with an idea of scaling up these materials at different length at this unreachable limit. NIMS has excellent research facilities. Thanks to this, we can use world most sophisticated apparatuses. We are producing variety of semiconductors with ultra narrow diameter (~1nm) according to our own purpose, inducing dimensionalities and attempting to connect them internally by metal electrodes without using lithography. In addition, axial heterojunctions at this scale will be attempted so that built in electronic components can be realized within a single nanomaterial. The ultra high density electronic component fabrication (parallel and crosswire communication devices, RAM, ROM and Memory devices exceeding terabit) with ultra-narrow single component nanowires is ongoing.The research, we are carrying out, yet to be explored by other groups at this low scale. Increasing functionality (complexity with desired target) and successful interconnection, exploring the inherent new physio-chemical properties, might open up new direction of research, which has been a long goal of nanotechnology.

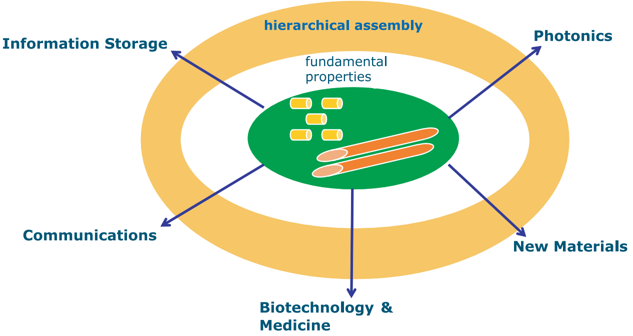

Fig. 1. Theme of materials research exploration with the ultra-narrow semiconductor building blocks.

2. Research Activities

(1) Multidimensional quantum Gold assemblies[1)]

The multidimensional assemblies of quantum gold particles built into 0D, 1D & 2D dimensions show tunable surface plasmon resonance that can be applied to other nanomaterials for facile manipulation of assembly processes permitting an exploration of physicochemical properties as well as technological applications.

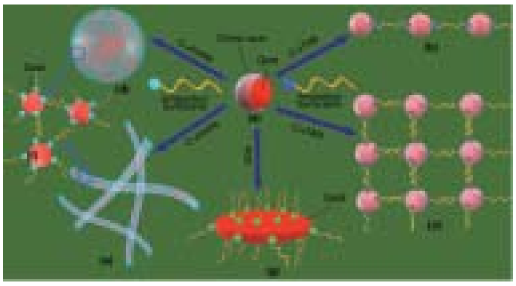

Fig. 2. Multidimensional assemblies of quantum gold particles.

(2) Nanorod Driven Polarization-Tailored Electro-optic Devices[2,3)]

Novel soft matter type blend of ultranarrow ZnS nanorods and nematic liquid crystal shows previously unachieved and rapid electro-optic properties. The work has been patented. The blend shows tunable polarizations from vertical to grazing view angles with a significant adjustable anisotropy for improvement of contrast ratios and viewing angles of LC displays.

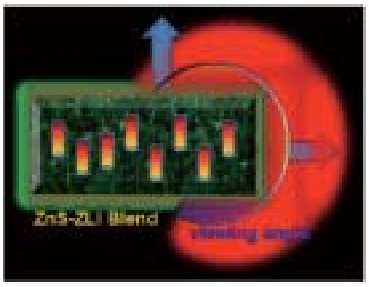

Fig. 3. A schematic of nanorod-liquid crystal blended cell with improved viewing angle and contrast ratio.

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Organic Nanostructured Materials

ICYS-MANA Researcher **Richard CHARVET**

1. Outline of Research

Order between donor and acceptor components is a critical issue in the hot field of bulk-heterojunction organic solar cells. Indeed, the performances of such photovoltaic devices are highly limited by the nanomorphology of the photoactive layer. Free charges generated at the interface between donor and acceptor components usually get trapped or can not reach the anode and cathode electrodes as a result of poor ordering between the components and lack of precise pathways for charge migration. Although charges generation can be very efficient in organic solar cells, if the free charges can not reach the electrodes, then no electrical current is established.

We wished to improve the charge transport properties through the preparation of highly and precisely ordered organic materials. Thus, during my stay at MANA, the major part of my work involved the challenging preparation of functional discrete nanostructures containing well-ordered electron-donor porphyrin and electron-acceptor fullerene moieties. My work involved a lot of exploratory design for molecules and macromolecules that could fulfill our objectives.

2. Research Activities

(1) Photoconductive 2D-linear porphyrin-fullerene dyad assembly by the Langmuir-Blodgett technique (collaboration with Dr. Somobrata Acharya)

Uniaxial compression of a stable Langmuir film at the air-water interface promoted aggregate formation of strategically designed amphiphilic porphyrin-fullerene dyad building blocks irreversibly as indicated by the large hysterisis between the compression and expansion cycles. AFM analysis of the compressed layer transferred on a mica surface revealed the formation of uniform aligned continuous domains in the form of nanowires over ~30 x 30 μm^2 with practically no void space (Fig. 1). The aligned nanowires exhibit remarkable end-to-end registry along with the side-by-side registry practically without any deviation over two micron range retaining ~1.3 nm width of the nanowires. The nanowires in the hierarchical array have very high aspect ratio exceeding 10^3 with very tight registry.

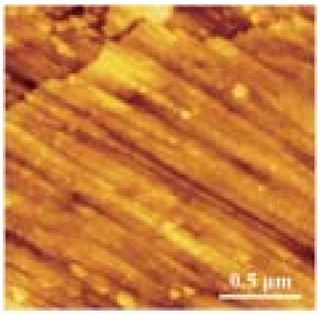

Fig. 1. AFM image of a LB monolayer.

Monitoring of the aggregation process by on trough reflection spectra in the UV-visible range as a function of the applied pressure showed the formation of porphyrin J-aggregates upon compression.

To evaluate the electrical properties, 2-mm gap silver electrodes were deposited by sputtering using a mask on a 10-layer LB film. These nanostructures were found to be photoconductive and photocurrents as high as 10 μA could be observed upon white-light irradiation.

(2) High-mobility photoconductive anisotropic nanowires of tunable dimensions via self-recognition of block copolymers

High-mobility photoconductive nanowires with tunable dimensions and properties could be prepared by the self-assembly of a new family of rod-like block copolymers appended with hydrophilic porphyrin side chains in one block and hydrophobic fullerene moieties in the other block. These nanowires formed by simple drop-casting on most surfaces thanks to a selective self-recognition process between similar polymer blocks generating stacked supramolecular p-n junctions within each nanowires (Fig. 2). The diameter of the nanowires can be controlled by changing the polymer chain length while the internal spacing between self-assembled polymer chains is tunable upon variation of the length of the fullerene side-chains. TEM and in-plane XRD-analysis indicated that the nanowires consisted of alternating discrete domains arranged periodically perpendicular to the long axis of each nanowire, indicating a preferred growth direction along the long axis. Thanks to the specific supramolecular organization of the photoactive components, remarkable photoconductive properties and high charge carrier mobility (0.26 $cm^2V^{-1}s^{-1}$) have been obtained.

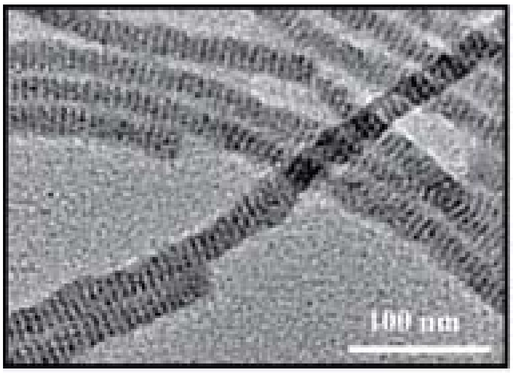

Fig. 2. TEM image of self-assembled nanowires.

Universal Semiconductor Diagnosis Using Multi-dimensional EBIC Technique

ICYS-MANA Researcher Jun CHEN

1. Outline of Research

The advancement of Si device technology is the fundamental of Japanese industrial development. The MOSFET using high-k/metal gate stack is expected for the Si memory devices of next generation due to reduced leakage current and compatible for future scaling. Recently, several US companies have committed to putting hafnium-based high-k gate dielectrics and metal gate electrodes into production for the 45 nm generation. Thus, we have to accelerate the speed of research by optimizing the device fabrication process. For accelerating the optimization of fabrication process, it is indispensable to have a suitable characterization technique to check the reliability of actual high-k devices.

The technology of the device become more complicated and the function of device has no longer come from the distinguished character of one material but from the hybrid structures. For such new materials and devices, conventional characterization tools are almost closed to their limits, and new tools should be developed. Here, I propose a multi-dimensional electron-beam-induced current (EBIC) technique for this purpose.

EBIC technique is a versatile tool to image the defects in semiconductors and/or to find the failure in the actual devices. We are aiming to apply this technique for the future advanced semiconductor devices. Parametric observations with temperature-, beam energy-, bias- and time-dependences will be established on testing element group (TEG). This EBIC technique has two big advantages, first is the direct observation of actual devices and second is a comprehensive characterization of leakage properties in both micro- and macro- scale.

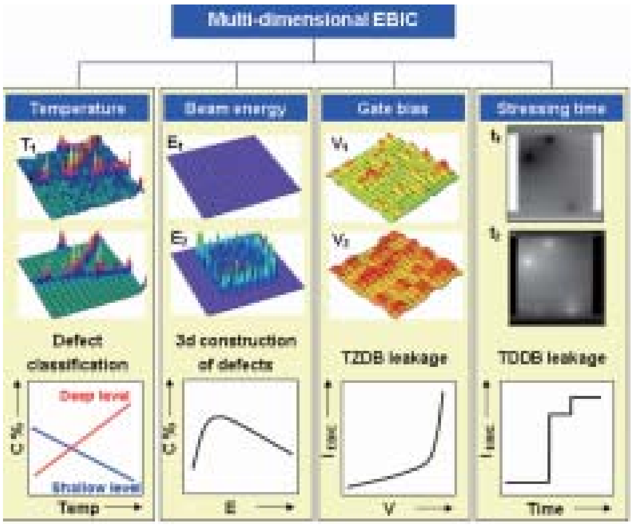

Fig. 1. The concept of multi-dimensional EBIC characterization.

2. Research Activities

(1) Failure analysis of high-K/metal gate MOS [1)]

We have demonstrated the visualization of the leakage path in high-k dielectric film for the first time by EBIC and as far as we know, it is the only way to visualize the leakage sites in the high-k gate stack (Fig. 2). Significant difference between p- and nMOS are found. That is, pMOS contains very high density of leakage sites, which are located not only in the edge but also in the center. The EBIC results can give a strong hint of the different leakage and breakdown behaviors in p- and nMOS. The type of gate electrode plays an important role in the leakage behavior in pMOS. High density of charged traps was found in pMOS with p+poly-Si or TaSiN gate electrodes. For the application of high-k, fabricating perfect pMOS is still a challenging task.

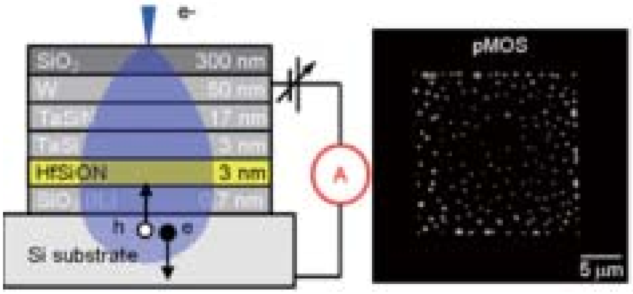

Fig. 2. The cross-sectional structure of MOS capacitor with high-K/metal gate (left). Top-view EBIC image of leakage sites in pMOS.

(2) Study of grain boundaries in solar-grade Si [2)]

We have clarified the residual strain and electrically active grain boundaries (GBs) in multicrystalline Si used for solar cells. The former concerns the process yield and the latter affects the solar cell efficiency. The distribution of strain was imaged by scanning infrared polariscope (SIRP) and the electrically active boundaries were characterized by EBIC. Large strain was detected near twin boundaries and small-angle GBs. Twin boundaries are electrically inactive, while SA-GBs act as strong recombination centers. It indicates that the electrical activities of GBs are not directly related to the residual strain.

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One-dimensional (1D) ZnS Nanostructure-based Fundamental Properties and Applications

ICYS-MANA Researcher Xiaosheng FANG

1. Outline of Research

One-dimensional (1D) nanostructures have recently stimulated great interest due to their potential value for understanding fundamental physical concepts and for applications in constructing nanoscale electric and optoelectronic devices since the discovery of carbon nanotubes.[1)] 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. In our past research, we have successfully been synthesized 1D ZnS nanostructures with various morphologies and their assemblies in well-controlled and simple ways. Some facile and effective routes have been developed to enhance their field-emission properties and to tune optical behaviors, including photoluminescence (PL) and cathodoluminescence (CL).

The purpose of our current research is to initiate the studies on fundamental properties and aplications based on 1D ZnS and nanostructures or heterostructures, which will primarily focus on the investigation of their novel optical property, the fabrication of ultraviolet (UV) and gas sensors with high performances. In detail three sub-themes are planned: (Fig.1)

(i) Understanding the principles of controlled growth and elucidation of fundamental physical properties of 1D ZnS nanostructures with various morphologies, 1D ZnS nanostructure-based hierarchical nanostructures, heterostructures and doped nanostructures.

(ii) Development of 1D ZnS nanostructure-based UV sensors with high performances based on detailed studies of their novel fundamental physical properties.

(iii) Exploration of efficient 1D ZnS nanostructure-based gas sensors through functionalizing its surface or doping.

Fig. 1. Illustration of the objectives of proposed research.

2. Research Activities

(1) Multi-angular Branched ZnS Nanostructures with Needle-shaped Tips: Potential Luminescent and Field-Emitter Nanomaterial.[2)]

A facile and effective route toward the synthesis of ZnS multi-angular branched nanostructures with needle-shaped tips has been developed. An average width of the structurally and chemically uniform, single-crystalline, defect-free tips was found to be less than 10 nm. Cathodoluminescence from individual ZnS multi-angular branched nanostructures was investigated at high spatial resolution on the nanometer scale. The size-dependent optical spectra exhibit sharp ultraviolet bandgap emission and broad visible emission. Field-emission measurements show a relatively low turn-on field of ~ 3.77 V/μm at a current density of 10 μA/cm^2 and the highest field enhancement factor β of ~2182 ever reported for 1D ZnS nanostructures. This was attributed to the specific sharp tips and high aspect ratios.

(2) Structure and Cathodoluminescence of Individual ZnS/ZnO Biaxial Nanobelt Heterostructures.[3)]

We report on a controlled synthesis of two novel semiconducting heterostructures: hetero-crystalline- ZnS/single-crystalline- ZnO biaxial nanobelts and side-to-side single-crystalline ZnS/ZnO biaxial nanobelts via a simple one-step thermal evaporation method. High-spatial resolution cathodoluminescence (CL) studies on individual heterostructures for the first time reveal a new ultraviolet emission peak (~ 355 nm), which is not observed in separate ZnS or ZnO nanostructures. (Fig.2)

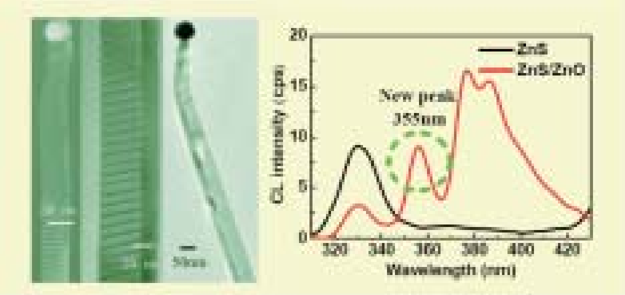

Fig. 2. ZnS/ZnO Biaxial Nanobelt Heterostructures and their new UV peak.

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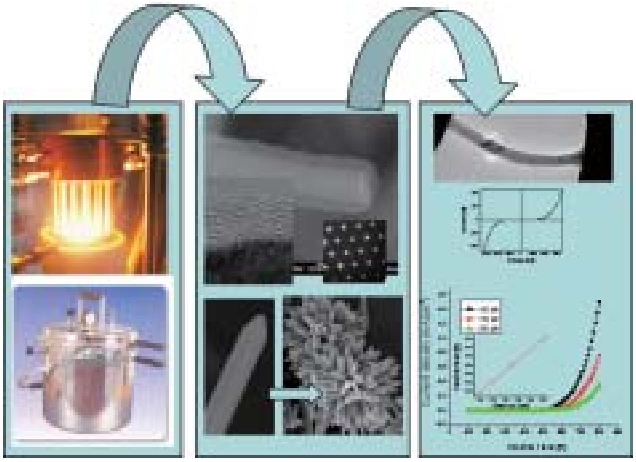
Investigation of Growth and Properties of ZnX (X=O, S) Nano/heterostructures and Thin Films

ICYS-MANA Researcher **Ujjal K. GAUTAM**

1. Outline of Research

We are interested to investigate the synthesis of functional 1D nano and heterostructures such as CNT-ZnS, CNT-In, ZnS-ZnO etc. Such heterostructures provide a new set of materials with combined properties from both the constituent materials. Details of their growth and intrinsic properties will be investigated. Additionally, we undertake efforts for N doping of ZnO nanocrystals which is very important for inducing P type behavior in ZnO. The intrinsic properties of a material, such as microstructure, local and global electronic structure, distributions of its defects etc. could be attributed to materials growth. Thus, effort has been dedicated to understand the growth of these materials and its relation to non-uniformities within a nanostructure, using high spatial resolution cathodoluminescence investigations. Surface energy tailoring is an effective way to control morphology, which is often achieved by using capping agents. We have investigated the possibility of the same by dint of doping, because the adatoms can modify surface energies.

Towards the end of the first year, I also propose to begin investigation of growth of single-crystal thin-films by employing liquid-liquid interface. This is distinctly different from all other techniques, since this employs chemical reaction-induced crystallization confined solely to the interface region. Due to this special feature, we were able to obtain single-crystal thin films, whose thickness can be as less as 5 nm, and width up to several centimeters, at room temperature.



Synthesis → growth investigation → properties

Fig. 1. Three sub-themes with their coordination for investigating growth, properties and applications of 1D nano and heterostructures.

2. Research Activities

(1) Synthesis of 1D heterostructures:

We have synthesized several 1D heterostructures, such as ZnS-CNT core-shell heterostructures1), carbon coated In-ZnS hierarchical heterostructures, and In-ZnS heterostructures within a carbon nanotube. The single-crystalline ZnS content inside a carbon nanotube improves the mechanical strength of the nanotubes. In nanowires inside a ZnS nanotubes retains its bulk superconductivity in one dimensional limit, due to surface passivation (Fig2)2).

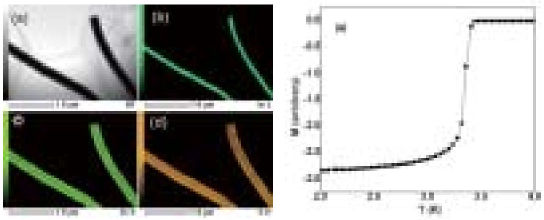


Fig. 2. EDS mapping of In core, ZnS shell heterostructures and their magnetization vs. temperature curve.

(2) Developing solution routes for Nitrogen doping in ZnS:

N doping is generally achieved at very high temperatures using vapor phase CVD techniques which is not suitable for nanostructures. We have developed a novel solvothermal technique, where ammonia was used the N precursor3). N doping greatly enhances the electrical conductivity leading to high field emission current from these nanostructures.

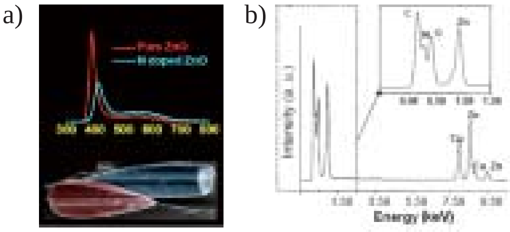


Fig. 3. (a) ZnO nanobullets doped with N, the comparison of the pure and doped emission spectra are shown in inset (b) EDS spectra acquired from a N doped nanobullet.

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Structure Analysis and Properties of Quasicrystals and their Approximants

ICYS-MANA Researcher **Cesar P. GOMEZ**

1. Outline of Research

Complex Metallic Alloys (CMAs) 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 (Fig. 1).1) However, most quasicrystals are not binary but ternary, and thus often suffer from partial chemical order/disorder. We must thus answer a second question: ”which atom is where?”. Thus, in order to expand the structure model of the parent binary Yb-Cd quasicrystal to the ternary members of the same family, the model needs to be amended with information of chemical order which can be obtained by studying different approximant phases in related ternary systems.

There are three known families of icosahedral quasicrystals; Mackay-, Bergman- and Yb-Cd-type phases. When the appropriate building blocks are considered, it is seen that these families are more closely related than previously imagined; the Yb-Cd-type and Bergman-type phases can be described using the same set of building blocks in the same arrangements. The only difference between these two families is the atomic decoration within these building blocks. Therefore this project also aims at establishing a general framework for describing structures of icosahedral quasicrystals.

We are also aiming at synthesizing new quasicrystals and approximants with interesting physical properties. Potential fields of application for these CMAs involve surface coatings with low heat conductivity, low friction and wear. They also have a high potential for thermoelectric applications.

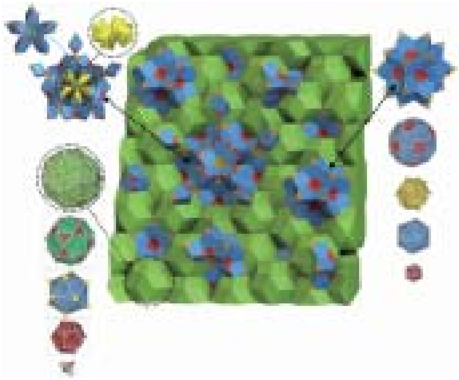

Fig. 1. A slab of the YbCd5.7 icosahedral quasicrystal. The image shows the different building blocks in the structure and their atomic decorations. Yb atoms are seen in yellow and Cd atoms in grey.

2. Research Activities

(1) Synthesis, Analysis of Structure and Chemical order in ternary Yb-Cd-related CMAs:

Alloy samples are prepared by high-temperature reactions of pure metals under inert atmosphere. The samples can sometimes be grown directly from the melt or by using a self-flux method. The analyses 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. 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.

(2) Structure and formation mechanisms of Bergman-type CMAs:

The recently found Bergman phases in the TM-Mg-Zn systems (TM=Hf, Zr, Ti) are the only F-type (face centered icosahedral) quasicrystals of this family that also have related approximants. The atomic structures of these phases have been studied by X-ray diffraction and their formation described in terms of chemical intergrowth of related Laves phases (Fig. 2).2) The analyses of the approximant phases in the TM-Mg-Zn have enabled further understanding of the quasicrystals in the same systems. Phase-reconstructed electron density maps obtained by LDE (Low Density Elimination) of the actual quasicrystals reveal that they contain the same atomic clusters as the approximants.

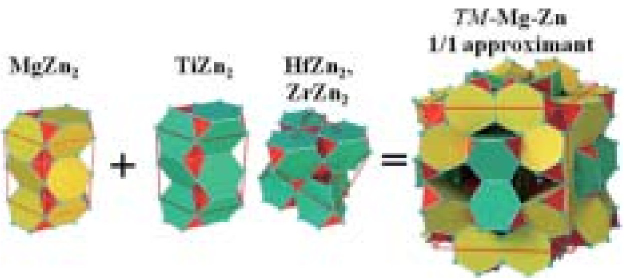

Fig. 2. TM-Mg-Zn (TM=Hf, Zr, Ti) approximants described as a chemical intergrowths of related Laves phases.

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Deep-ultraviolet Diamond-based Photodetector for High-power Excimer Lamp

ICYS-MANA Researcher Masataka IMURA

1. Outline of Research

The next generation photolithography system, which uses a stepper with an excimer laser such as an ArF laser (λ=193nm) and an F2 laser (λ=157nm), 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^+-diamond (100) substrates.

2. Research Activities

(1) Crystal growth and device fabrication[1,2]

The p-diamond epilayers were homoepitaxially grown by microwave plasma chemical vapor deposition (MPCVD) on the heavily B-doped p^+-diamond (100) substrates commercialized by Technological Institute for Super-hard and Novel Carbon Materials (TISNCM). The substrate was 2.5 × 2.5 × 0.5 mm^3 in size, and the B concentration ([B]) was measured to be around $1{\times}10^{20}$ cm^{-3} by secondary-ion mass spectroscopy (SIMS). The unintentionally B-doped p-diamond epilayers with [B] in the range 10^{15} to 10^{16} cm^{-3} analyzed by SIMS were grown by CH_4 and H_2 gases. The ratio of CH_4 to H_2 was 0.08 %, and the corresponding flow rates of CH_4 and H_2 were 0.4 and 500 sccm, respectively. The reactor pressure was fixed at 106 hPa during growth. The growth was performed at ~800 °C. The thickness of epilayer was about 0.5 μm.

Figure 1 shows the schematic illustration of the device structure of vertical-SPD. 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 °C 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.

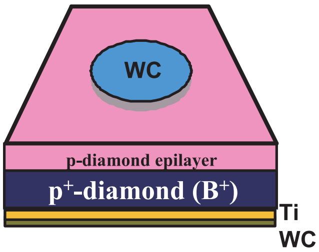

Fig. 1. Schematic illustration of diamond-based SPD.

(2) Photoresponse property

Figure 2 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 10^{-14} A. The rectification ratio is determined to be around 10^{12} at ±3 V. The ideality factor (n value) of the SPD is 1.1, and the Schottky barrier height is determined to be 1.42±0.01 eV. The SPD is operated in only the reverse bias mode. The photocurrent is almost constant with increasing the reverse bias voltage.

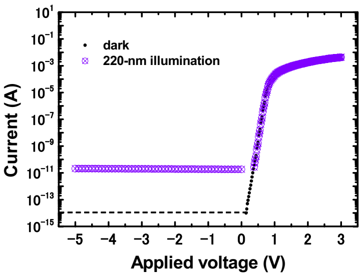

Fig. 2. Dark current and photocurrent under 220-nm light illumination as a function of applied voltage.

Figure 3 shows a dependence of responsivity at zero voltage on wavelength. Peak position is 188 nm.

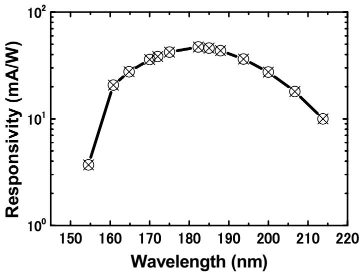

Fig. 3. Responsivity at zero voltage on wavelength.

Figure 4 shows a typical stability result by excimer lamp with 20 mW. The SPD has very stable.

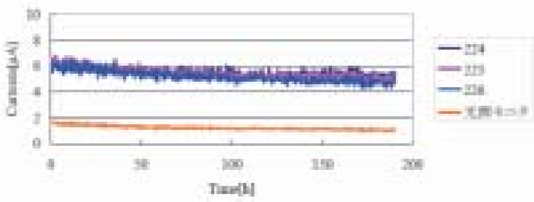

Fig. 4. Stability result by excimer lamp with 20 mW.

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Self-Assembling Conducting Polymers

ICYS-MANA Researcher **Michael V. LEE**

1. Outline of Research

Bottom-up fabrication has been an important concept for many years; however, progress to date has been limited principally to developing tools and expanding understanding of the underlying principles. Even though much progress has been made, nanoscale structures are still constrained in fabrication in the vertical direction.[1-4)] My project at ICYS is to combine some of the tools at our disposal to develop a practical system for fabrication at the nanoscale.

I will combine nanoscale 2D templates, custom self-assembling monomers, and electrochemical polymerization to form complex 3D nanoscale structures. Nanoscale patterning by photolithographic means and it's research counterpart, electron beam lithography, are the workhorses for patterning on a surface; they are able to pattern and form structures reliably within an order of magnitude above and below 100 nm. Self-assembly has been shown to form complex supermolecular structures based upon the interactions between individual molecules, forming ordered structures orders of magnitude larger than the molecules from which they were formed. Electrochemical polymerization can be used to form conductive polymers on a surface.

By combining these three tools we will form a practical method for fabricating 3D nanoscale structures. The 2D nanofabrication allows nanoscale control in the lateral directions. The self-assembling properties will allow the polymers to grow vertically from the surface without losing that resolution. Electrochemical polymerization conditions will enable nanoscale control over the growth in the vertical direction. An side-view of the expected initial structures is shown in Figure 1.

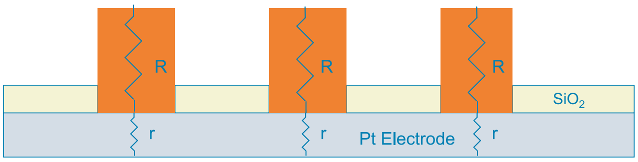

Figure 1. Side-view image of polymers growing from a platinum electrode. The electrode is patterned nanoscale with a SiO_2 mask.

2. Research Activities

In conjunction with Dr. Katsuhiko Ariga's (MANA-PI) Supermolecules group, monomers based upon the common 1, 8-diamminonaphthalene (18DAN) monomers have been developed, Figure 2. The monomers are modified with common functional groups useful for self-assembly. When these monomers are electrochemically polymerized, they are able to form different unique structures based on the self-assembling properties of the individual monomers.

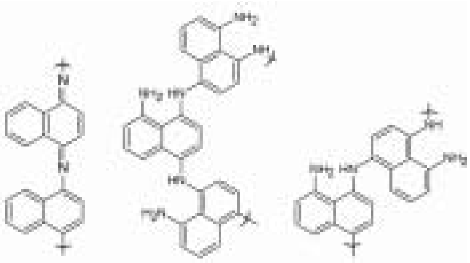

Figure 2. Three different structural blocks for 18DAN based polymer growth. The more oxidized form forms a linear chain. The leucoemeraldine form has two general options, helical or linear.

As can be seen in Figure 3, different monomers yield polymers with unique structural properties. By changing the self-assembling group, the polymer morphology changes from globular, gel-like growth to linear growth. The images show structures on the order of 100 nm, which meshes well with 2D nanoscale patterning. When grown from a nanoscale patterned electrode, they should yield functionalized 3D structures of defined and controllable nanoscale dimensions.

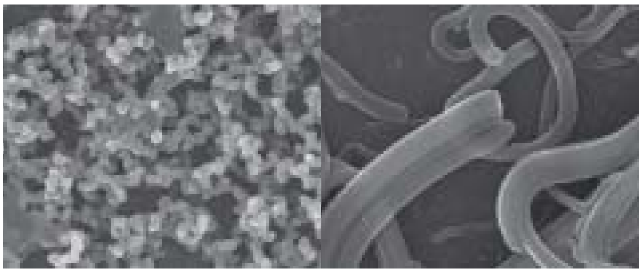

Figure 3. Electrochemical polymer growth with two different monomers. One shows gel-like globular growth, while the other shows replication of the polymer pattern below it. The features on the right have collapsed upon drying. The images are approximately 4 um x 4 um.

Once the principle has been demonstrated, the functional groups can be varied to produce structures with defined chemical functionality 3-dimensonally at the nanoscale. Such structures will be useful for biological assays, optical applications, electronics, and electrochemical sensors.

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Self-organized Atomic-scale Structures on Silicon Surface

ICYS-MANA Researcher Canhua LIU

1. Outline of Research

The fabrication methods of the microelectronics industry have been refined to produce even smaller devices, but will soon reach their fundamental limits. A promising alternative route to functional system with nanometer dimensions is the autonomous ordering and assembly of atoms and molecules on atomically well-defined surfaces. It is interesting to study the mechanisms of such self-ordering phenomena, which can be employed to create a wide range of surface nanostructures from metallic, semiconducting and molecular materials, as well as to study their novel properties that may be utilized in the coming future. One of my research purposes is to find novel artificial nanostructures with fascinating properties by using the self-assembling technique combined with a surface geometrical template. In the near future, my research aim is to fabricate a novel magnetic nanostructure, which may contribute not only to our further fundamental understanding of low-dimensional physics, especially magnetism in reduced dimensionality, but also to the development of spintronic devices.

There are four correlated parts in my whole study surrounding the atomic-scale structures self-organized on Si surfaces (Fig. 1). The first is to fabricate atomic-scale structures on geometrically anisotropic silicon surfaces; The second is to visualize both atomic and electronic structures of the fabricated structures, not only to find out the mechanism of the self-organization process, but also to disclose various fascinating physical phenomena due to the reduced dimensionalities; The third is to measure physical properties of the fabricated structures, especially to focus on their magnetic properties, which is of importance to the last part of my research – to develop novel magnetic devices, or in other words, to utilize the self-organized atomic-scale structures with their new functionalities to be discovered.

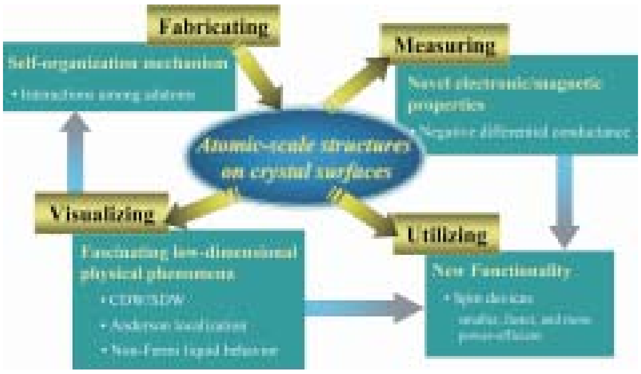

Fig. 1. Schema of the research work surrounding atomic-scale structures self-organized on crystal surfaces.

2. Research Activities

(1) *Self-assembly of Co adatoms on In atomic-scale wires due to indirect adatom-adatom interactions mediated by substrate electron gas*[1)]

Low-density Co atoms are found to self-align on the Si(111)-4×1-In surface in the direction of In atomic wires (Fig. 2). Indirect interaction between a pair of Co adatoms is revealed to be mediated by a quasi-one-dimensional electron gas confined within the In atomic wires.

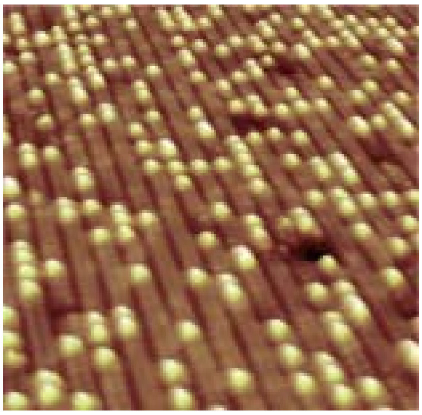

Fig. 2. A typical STM image of array of self-aligned Co adatoms (bright protrusions) along In atomic-scale wires. Width of the In wire is 1.33 nm.

(2) *Impurity-induced Phase modulation of quasi-one-dimensional charge-density waves*

The array of In atomic wires, the Si(111)-4×1-In surface, condensates to a charge-density wave (CDW) state when being cooled below ~120 K. With STM, we succeeded in observing the CDW phase modulation induced by the Co atoms adsorbed thereon through scattering electrons (Fig. 3). Our STM observations provide direct evidence for the existence of static solitons and phase flips resulting from interactions between defects and CDW state.

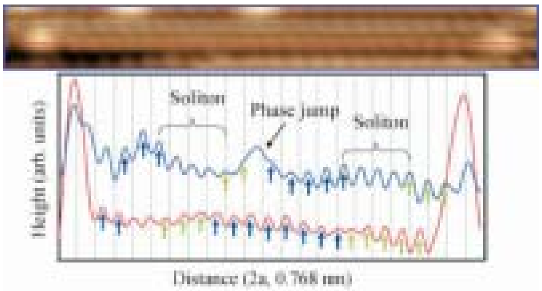

Fig. 3. Line profiles taken from the lines indicated in the upper STM image, showing CDW phase modulations as arrows indicate.

Reference

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Ab initio Molecular Dynamics in Nanotechnology

ICYS-MANA Researcher **Roberto SCIPIONI**

1. Outline of Research

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 re-calculations 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 nano architectonics for theoretical researchers and experimentalists alike.

2. Research Activities

a) Recently a big interest has been devoted to the study of water solutions containing different solutes like Na and Cl which have incredible relevance at biological level. The effects of the ions on the hydrogen bond network has been investigated using a big system containing 128 molecules for a simulation time of up to 23 ps within an ab initio simulation scheme. Interesting results have been obtained for the dipole moments and related quantities. See for example Fig1.

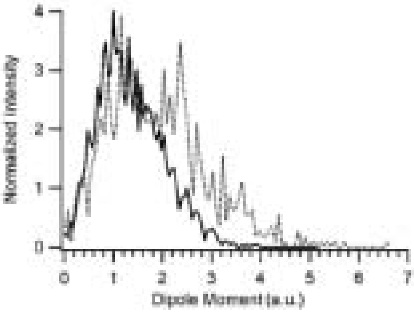

Fig. 1. Distributions of dipole for water molecules for pure water (dashed) and a solution containing 0..43 M of NaCl (solid) (from [1]).

b) Recently interesting molecules have been discovered which can be considered complimentary to fullerenes with respect to their ability to interact with electrons. The molecule shown in Fig 2 is an interesting candidate as a precursor for fullerenes and it possesses unique symmetry features.

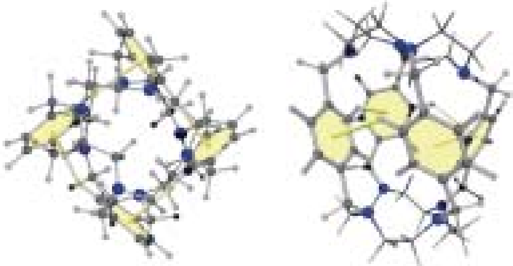

Fig. 2. New found molecular structure of $C_{48}N_8H_{64}$ confirmed using ab initio finite temperature Car Parrinello Molecular Dynamics (from [2]).

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Development of Nanosheet Seed Layer Technique for Oriented Film Deposition

ICYS-MANA Researcher Tatsuo SHIBATA

1. Outline of Research

Thin film technology is one of the most essential technologies which support today's electronic and optelectronic devices, and thus, it is crucially important to develop a technique to control film growth of various functional materials. Recently, I have proposed a new method to obtain oriented film growth using two-dimensional crystals named "nanosheet" as seeds. (1) Nanosheets have been synthesized by delamination of layered host materials into colloidal single-sheets via soft-chemical procedure. Nanosheets have notably high two-dimensional anisotropy with an ultrathin thickness of around 1 nm. They inherit high crystallinity from layered precursors, and an individual nanosheet can be considered as a two-dimensional single crystal. Using this unique two-dimensional crystal surface, an extremely thin seed layer could be fabricated. Since the film growth is strongly dominated by the surface structure of substrates, unilamellar nanosheets deposited by simple wet-coating method at room-temperature could promote oriented crystal growth of sol-gel deposited oxides.

In this research, I plan to develop a low-temperature (especially room-temperature) film fabrication method by utilizing this "nanosheet seed layer technique"(Fig. 1). The goal of this research is to fabricate well-crystallized and orientation controlled functional crystal films onto flexible substrates such as plastics. To accomplish the objective, following three subjects will be studied.

(i) Establishment of low-temperature film fabrication on nanosheet seed layer

(ii) Enrichment of nanosheet (seed material) library

(iii) Improvement of nanosheet deposition technique (deposition on plastics, pattering of nanosheet seed layer etc.)

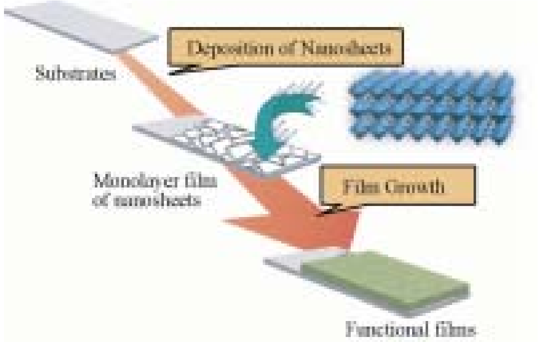

Fig. 1. Schematic explanation of nanosheet seed layer technique.

2. Research Activities

(1) Development of film fabrication by pulsed laser deposition on nanosheet seed layer

PLD is a one of the most desired techniques for low-temperature film fabrication of various crystals, because it can provide film precursors with high kinetic energy. Thus, I tried to utilize the method to fabricate oxide films on the nanosheet seed layer. Using a perovskite-related nanosheet ($Ca_2Nb_3O_{10}$ nanosheet) as a seed material, a highly crystallized and (100) oriented $SrTiO_3$ was successfully grown on the nanosheet seed layer substrate, suggesting that this technique is also effective for PVD process.(Fig. 2)

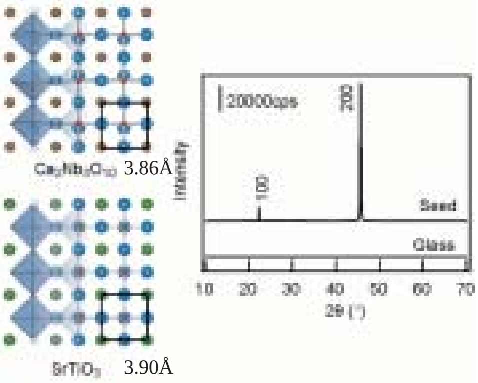

Fig. 2. Schematic illustration of the surface structure of $Ca_2Nb_3O_{10}$ nanosheet and $SrTiO_3$ (100) plane, and XRD patterns for $SrTiO_3$ films deposited at 550°C.

(2) Screening of new nanosheet seed materials

To control the orientation of a crystal film with a hexagonal structure is strongly desired, because a number of important materials such as ZnO and GaN adopt this symmetry. For this purpose, nanosheets which have a two-dimensional hexagonal lattice were examined, and oriented growth of ZnO crystal along c-axis was successfully achieved on MnO_2 nanosheet seed layer in spite of a rather large lattice mismatch.(Fig. 3)

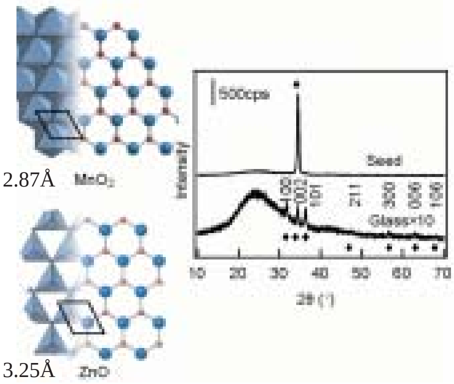

Fig. 3. Schematic illustration of the surface structure of MnO_2 nanosheet and ZnO (001) plane, and XRD patterns for sol-gel derived ZnO films obtained by heat treatment at 400°C.

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Synthesis of Organic Materials using Porous Alumina Template

ICYS-MANA Researcher **Yasuhiro SHIRAI**

1. Outline of Research

The objective of our research is the development of nanostructured organic materials producing novel and unique properties, with which we can possibly realize ultra-dense, efficient, cost-effective, and/or environmentally friendly electronic and optoelectronic devices. The key is the reduction of the dimensions with the precise control of nanostructured organic materials.

Conducting plastics have significant advantages over their inorganic counterparts because low-cost, large-area, and flexible devices can be possibly achieved. However, the serious bottle-neck has been the low mobility of electric carriers in organic materials, especially in polymeric materials. We will explore the strategies to solve this problem using porous alumina template assisted synthesis of polymeric nanowires (Fig.1).

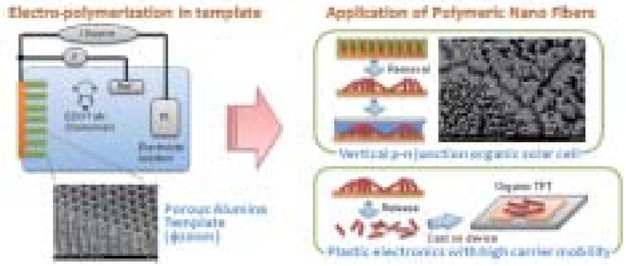

Fig. 1. Template-assisted synthesis of Polymeric Nano wires.

2. Research Activities

(1) Synthesis and Measurements of PEDOT Nano-wires

Possibility of controlling morphology of polymer chains in conductive polymeric materials is explored. 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 (Fig. 2).

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 nanoprobing system 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.

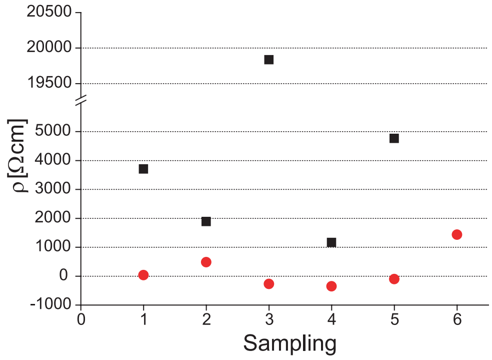

Fig. 2. Electrical resistivity of the PEDOT nanowires. PEDOT nanowires with the diameter of 30nm (red circle) and 60nm (black square).

(2) Synthesis of Vertical p-n junction plastic solar cell

Conjugated polymer-based photovoltaic devices have been considered promising materials for achieving cost-effective and high-performance photovoltaic devices. The bulk heterojunction devices can accomplish the enhancement of the donor-acceptor interfacial area by simply mixing the donor-acceptor materials in a common solvent, and give best power conversion efficiency. However, control over morphology of the donor-acceptor materials is minimal. To further improve the power conversion efficiency of organic solar cells, it is important to control the interface between the donor-acceptor materials to accomplish high donor-acceptor interfacial area as well as efficient charge transport path.

To achieve this goal, we have developed methodology to synthesize organic thin films with nanoscale vertical p-n junctions. We have successfully produced polymer nanofiber forests on electrode surface by using nano-sized porous alumina template and electrochemical polymerization techniques. The empty spaces within the nano-fiber forest were then filled with N-type organic materials such as C60 and PCBM, thus creating vertical p-n junctions between the nano-fibers and filling materials. (Fig.3)

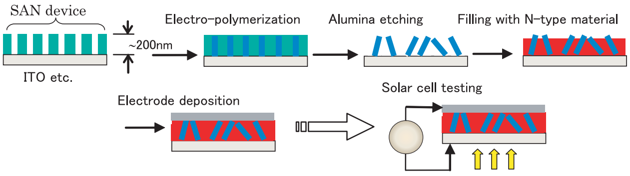

Fig. 3. Plastic solar cell fabrication using porous alumina template.

Reference

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Development of Novel Nanoporous Materials for Electrochemical Applications

ICYS-MANA Researcher Pavuluri SRINIVASU

1. Outline of Research

Ordered mesoporous carbon materials are potentially of great technological interest for the development of electronic, catalytic, hydrogen-storage systems and adsorption of biomolecules[1-2].

Porosity in the carbon materials can be generated by various processes including activation of organic precursors, carbonization of polymers at high temperature and carbonization of organic molecules inside the porous matrix of inorganic templates. Among them, templating process is very attractive and highly successful for making well ordered porous carbon materials with very high surface area and pore volume. The textural parameters of the nanoporous carbon materials are critical in many industrial applications particularly, separation, adsorption and fuel cells. The present study is focused on (i) the preparation ordered nanoporous carbon with high surface area and pore volume which can allow fine dispersion of nano particles using a small organic molecule namely glucose as a carbon source and (ii) preparation mesoporous silica using microwave-assisted high temperature technique. Mesoporous carbon was prepared using a hard templating approach using mesoporous silica as a template.

2. Research Activities

(1) Ordered nanoporous carbon and their applications:

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. 1). The specific pore volume is in the range of 0.93-1.51 cm^3/g and pore diameter in the range of 1.6-2.3 nm. The specific surface of MCG-0.75 is 1384 m^2/g and increases to 2073 m^2/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, mesoporous carbon with different loading of platinum has been made using chloroplatinic acid as a Pt source using wet impregnation. To reduce the use of amount of noble metal several efforts were made and 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 was observed 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. In conclusion, high surface area nanoporous carbon can give high dispersion of noble metals, which can help to prepare more viable and efficient fuel cells.

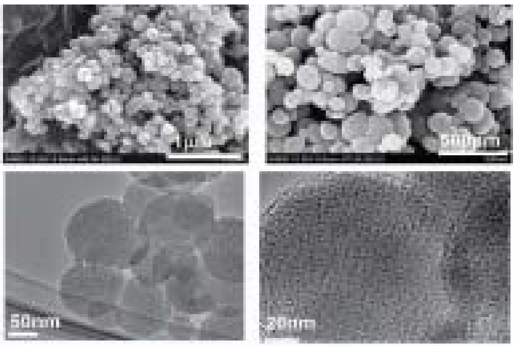

Fig. 1. HR-SEM and TEM images of MCG-1.0 material.

(2) Novel approach for the preparation of mesoporous silica using microwave-assisted high temperature technique:

Nanoporous materials synthesized using hydrothermal conditions is time consuming process. Microwave-assisted synthesis of mesoporous materials is a new area of research and offers several advantages than hydrothermal synthesis due to its rapid and uniform heating of the synthesis mixture. It has been found that the mesoporous materials with pore diameter in the range of 4-10 nm can be prepared by tuning the microwave synthesis temperature. It has also been found that the pore diameter of the materials is increased up to 10 nm at the expense of the specific surface area (Fig.2). In addition, the length of the unit cell constant increases from 16.62 to 21.85 nm with increasing microwave temperature. From the microscopic results, it is found that the material clearly exhibits highly ordered mesoporous networks with a regular mesopores and walls (Fig.2).

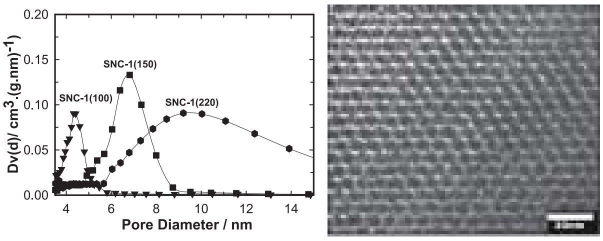

Fig. 2. BJH pore size distribution and HR-TEM image of mesoporous silica materials prepared using microwave technique.

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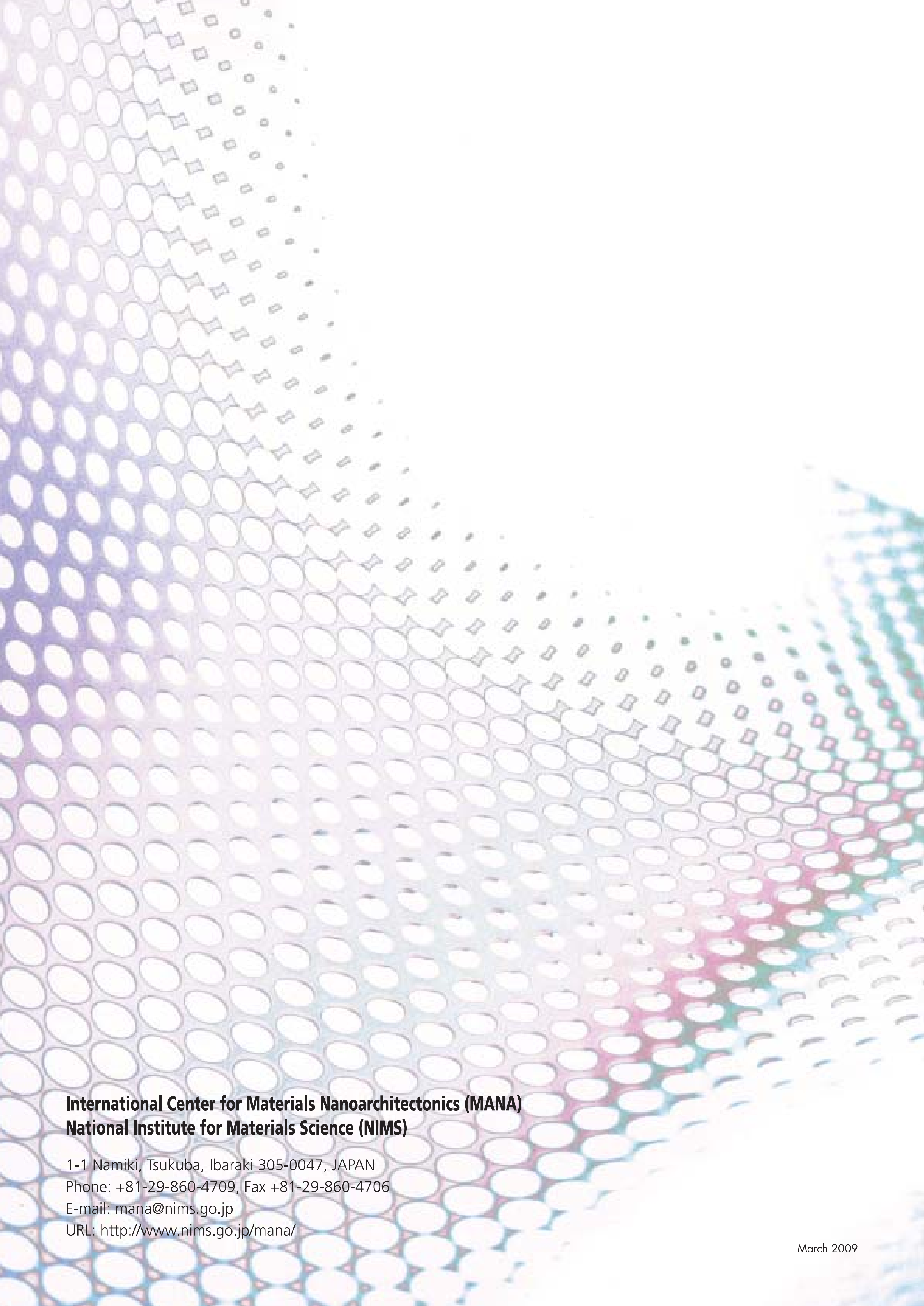

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