MANA
Progress Report

Research Digest 2009

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

National Institute for Materials Science (NIMS)

Preface

Masakazu Aono
MANA Director-General
NIMS

Two and a half years have passed since our International Center for Materials Nanoarchitectonics (MANA) was founded in the National Institute for Materials Science (NIMS) in October 2007 as one of five research centers approved/supported by the World Premier International Research Center Initiative (WPI Program) of the Ministry of Education, Culture, Science and Technology (MEXT). Thankfully, MANA has got off to a good start in both scientific research and administrative operation.

The aim of MANA is to carry out world topnotch research for the creation of novel materials necessary for the development of innovative technologies that are inevitable for the realization of the sustainable society in the 21st century. We are going to attain this goal on the basis of our new technology system referred to as ‘Materials Nanoarchitectonics’. The research in MANA is grouped into four areas, i.e., Nano-Materials, Nano-System, Nano-Green and Nano-Bio, although close collaboration among the four areas is regarded as most important.

This booklet, which is the part “Research Digest 2009” of the MANA Progress Report, summarizes the research activities of *MANA Principal Investigators*, *MANA Independent Scientists* and *ICYS-MANA Researchers* in the calendar year 2009. A *MANA Principal Investigator* is a 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 MANA Principal Investigators and other mentors. Other information on MANA research achievements (e.g., the lists of publications and patents) is given in the part “Management 2009” of the MANA Progress Report.

Lastly, on behalf of MANA, I would like to ask you for your continued understanding and support to MANA.

MANA Research Digest 2009

MANA Principal Investigators (30)

Nano-Materials Field

Nano-System Field

Nano-Green Field

Nano-Bio Field

MANA Independent Scientists (14)

ICYS-MANA Researchers (14)

Inorganic Nanosheets

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MANA Research Associate Jianbo Liang, Jia Baoping, Xiaoxiang Xu, Bui Thi Hang, Shibata Tatsuo, Akatsuka Kosho
Graduate Student Fengxia Geng, Baowen Li, Linfeng Hu

1. Outline of Research

We aim at developing a new nanofabrication process involving organization of 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 unique approach with nanosheets, we will establish the high designing ability and controllability over nanostructures with a nanometer-scale precision.

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 develop 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.

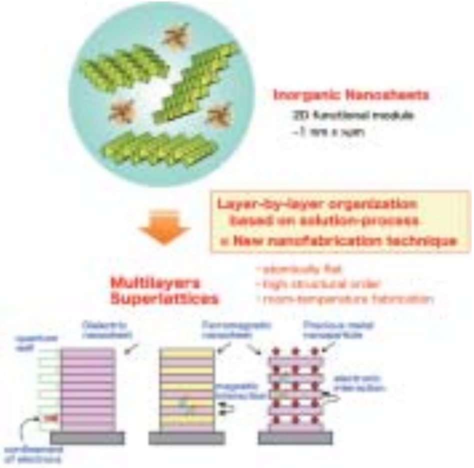

Fig. 1. Conceptual explanation of the research plan.

2. Research Activities

(1) Construction of Highly Ordered Multilayer Films of Titania Nanosheets[1)]

We have successfully deposited oversized nanosheets of $Ti_{0.87}O_2$ (1 nm in thickness x 10-20 μm in lateral size) into a neatly irganized monolayer film without large gaps and overlaps (see Fig. 2a) through Langmuir-Blodgett procedure. Repetition of this monolayer deposition produced highly ordered multilayer films (Fig. 2b), the structural order of which is comparable to that of artifitial lattice films constructed via beam epitaxy technique. The films are shown to be promising in applications as high-k nanofilms and sead layer for crystal film growth.

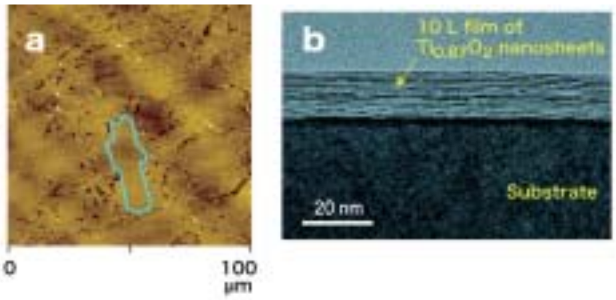

Fig. 2. a: AFM image of a monolayer film of $Ti_{0.87}O_2$ nanosheets. b: Cross-sectional TEM image of the 10 layer film. Outline in a indicates one nanosheet.

(2) Luminescent Films Fabricated from New Layered Rare-Earth Hydroxides[2,3)]

Platelet crystals of new layered rare-earth hydroxides, which we reported in 2008, could be self-assembled at the water/hexane interface, and be transferred onto a substrate into the oriented film (Fig.3). Heating the obtained hydroxide film at 800°C and above converted it into the oxide film in a topotactic fashion. Such films from Eu-doped Gd hydroxide exhibited enhanced photoluminescence properties, which are comparable to those for commercial Y_2O_3:Eu.

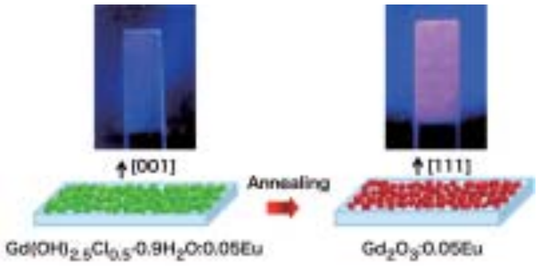

Fig. 3. Films of layered rare-earth hydroxides and oxide film converted from it by heating. Top photographs show the samples when excited by UV light.

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Supramolecular Materials

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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. Construction of molecular complexes for novel functions such as shape-modified fullerene assemblies,1) unusual chiral recognition,2) and anion-controlled charge separation3) was demonstrated as well as preparation of dimension-controlled nanomaterials.4) Various microscopic morphologies were successfully constructed through self-assembled process. Materialization of the self-assembled structures into hybrid systems resulted in selectivity-modified sensor system5) and nanowire-based photo-current device.6) Selected examples are shown below.

2. Research Activities

*(1) Chiral Sensing System by Achiral Indicator.*2)

Until now NMR spectroscopic detection of guest chirality using an achiral host has not been possible in the absence of a chiral medium or auxiliary since chiral discrimination is principally based on host and/or diastereomeric host-guest complex formation. We have demonstrated that an achiral oxoporphyrinogen works as a host capable of signaling chiral information of α-hydroxycarboxylic acids in ^{1}H-NMR spectroscopy (Fig. 1). In particular, enantiomeric excess (ee) can be determined by observing the splitting of ^{1}H-NMR resonances of the achiral host. This differs from the case of chiral hosts (shift reagents) where % ee is generally determined from the ratio of peak areas due to diastereomeric host-guest complexes. UV/vis, CD, FT-IR and NMR spectroscopic investigations suggest that the unusual phenomenon reported here is based on formation of a complex with 1 : 2 stoichiometry in concert with a protonation-driven tautomerization of host. This is the first example in which information about a chiral guest in a host–guest complex has been translated into information in the 1H NMR spectrum of an achiral host.

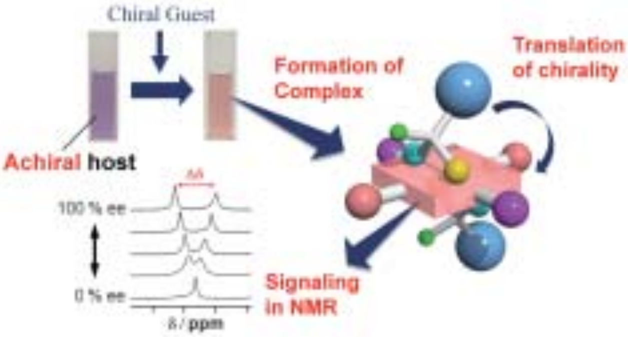

Fig. 1. Chiral sensing by 1H-NMR signals of achiral indicator.

*(2) Layer-by-Layer Films of Dual-Pore Carbon Capsules with Designable Selectivity of Gas Adsorption.*5)

Stable, homogeneous ultrathin films of uniformly dimensioned dual-pore carbon capsules with mesoporous walls and macroscopic empty cores were fabricated using layer-by-layer methods based on electrostatic interaction between polyelectrolyte and a surfactant coating of the carbon capsules. The resulting dual-porous carbon capsule films were investigated as a sensor substrate for vapors of different organic solvents. The carbon capsule films have much higher adsorption capacities than conventional electrolyte films and even than non-capsular mesoporous carbon films. The dual-pore carbon capsules have greater affinities for aromatic volatiles over their aliphatic counterparts, probably due to stronger π-π interactions. Additionally, the adsorption selectivity can be designed. Impregnation of additional recognition components into the carbon capsules permits further control over adsorption selectivity between aromatic and non-aromatic substances and between acids and bases in the prevailing atmosphere. Therefore, it is anticipated that the dual-pore carbon capsule films developed in this work will find application in sensing and separation applications because of their designable selectivity.

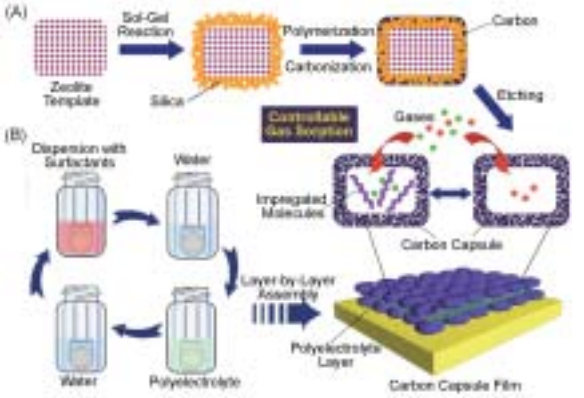

Fig. 2. Dual-pore carbon capsule film with designable selectivity of gas Adsorption.

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Inorganic Nanostructured Materials Group

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MANA Research Associate	Lang Li, Jing Lin, Chun Li, Haibo Zeng, Tianyou Zai

1. Outline of Research

Our ultimate goal is to explore various applications of one-dimensional nanomaterials, including their optoelectronic applications, composites materials fabrication etc. At current stage, we are developing controllable methods for synthesis of nanomaterials, investigating their properties, and developing novel nanofillers for polymeric composites to achieve mechanical reinforcement and thermal conductivity improvement.

In order to accomplish this purpose, we set up a full set of instruments for synthesis and characterization of nanomaterials, including induction furnace, transmission electron microscope etc, which enable us to effectively control synthesis of various nanotubes and nanowires. In addition, since we had many years' research experience on boron nitride nanotubes (BNNTs). Now we can synthesize large quantities of highly pure BNNTs. We are also trying to fabricate new 2D nanomaterials as nanofillers to achieve effective mechanical reinforcement and thermal conductivity improvement in composites. Based on the ultimate goal and our current researches, we set up following three sub-themes. (Fig.1)

(i) Developing highly effective synthesis method for various semiconductor nanomaterials;
(ii) Systematic property investigation to fabricated nanomaterials;
(iii) Developing highly thermo-conductive electrically insulating nanofillers for polymeric composites.

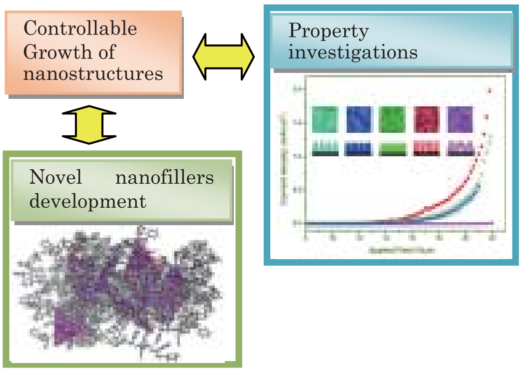

Fig. 1. Three sub-themes and their organic coordination.

2. Research Activity

(1) Novel nanofillers development — boron nitride nanosheets.[1)]

An efficient method was developed to fabricate highly pure 2D BN nanosheets in milligrams level. Their thicknesses can be as small as 1.2nm. Polymethyl methacrylate/BN nanosheets transparent composites were fabricated. The coefficient of thermal expansion for the composite films were remarkably reduced and a 22% improvement in the elastic modulus was obtained with only 0.3 wt% BN nanosheets fraction utilized.

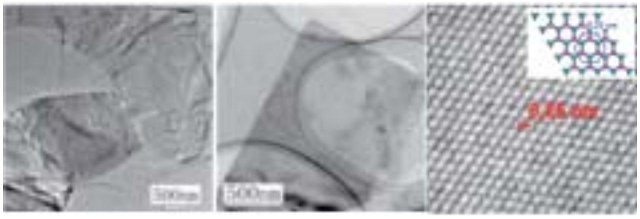

Fig. 2. TEM image of BN nanosheets fabricated. The most right image is high resolution image indicating the lattice and the inset is a scheme of atomic structure.

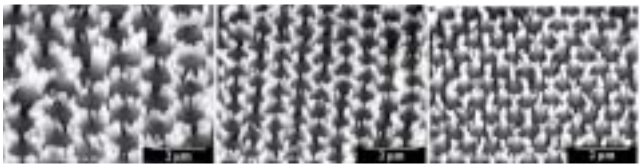

Fig. 3. SEM images of patterned ZnO nanorod arrays grown from1000 nm polystyrene plates with heating time of 0 min, 1 min, and 1.5 min, respectively.

(2) Controllable synthesis of ZnO and CdS nanowires and property investigations.[2,3)]

Methods were developed to synthesize ZnO and CdS nanowires in a controllable way. For ZnO nanowires, the nanowire density, uniformity and tapering were effectively adjusted to optimize their field electron emission. A very low turn-on field of 1.8 V/µm was finally realized. As for CdS structures, the microrods, sub-microwires, and nanotips were obtained in control, and their structural, cathodoluminescence and field emission properties were systematically investigated.

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Nanotube Properties

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1. Outline of Research

Opposed to well-established synthetic routes and deeply studied crystal structures, the exact physical properties of nanotubes, *e.g.* their intrinsic electrical and mechanical performance at the individual structure level, have remained basically unknown. The new techniques utilized by the Nanotubes Group, *i.e.* scanning tunneling microscope (STM) – transmission electron microscope (TEM) and atomic force microscope (AFM)-TEM, allow one for the first time to gain thoughtful insights into such properties under a full control of the tube morphology, its crystal and defect structure, and chemistry. The regarded works have been performed not only for the two basic nanotube systems, namely, C nanotubes (CNTs) and BN nanotubes (BNNT), but also for a variety of inorganic tubes made of various dielectrics and semiconductors.1)

2. Research Activities

(1) Electrical-field-assisted thermal decomposition of multi-walled BNNTs.

BNNT failure under a current flow is an important issue as far as its integration into nanoelectronics is concerned. We studied the Joule-heating-induced failure of an individual BNNT using the STM-TEM unit. The breakdown process occurred *via* thermal decomposition of tubular layers from inside-out of tubes leaving amorphous ball-like B-based nanoparticles behind (Fig. 1).2,3) Due to partially ionic nature of the B-N bond, the thermal decomposition temperature (1200-1900 K) was dependent on local electrical field: the higher the electrical field - the lower the decomposition temperature.

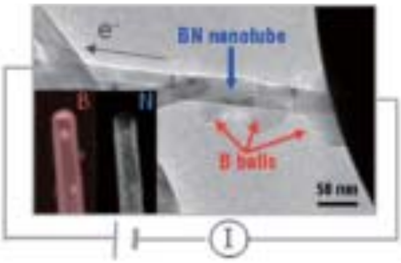

Fig. 1. An individual BNNT under a current flow in the STM-TEM; Growing B-balls are arrowed; they are also verified by the elemental maps taken from the decomposed tube (inset).

(2) Interface dynamic behavior between CNT and metal electrode.

Metal contact–NT interface dynamics is a crucial question in regard of the CNT electronics.4) The interactions between CNTs and W electrodes were analyzed in STM-TEM. Under current, the metal tip absorbed CNT atoms, which then penetrated deep into its body, formed a tungsten carbide, and finally precipitated as freshly-formed C tubular shells encapsulated the electrode. CNT wall-thickness shaping *via* stepwise absorption of the inner shells by the electrode was demonstrated. This work provided detailed understanding of the CNT catalytic growth and the previously unknown spatially-resolved kinetics at a given nanotube/metal interface.

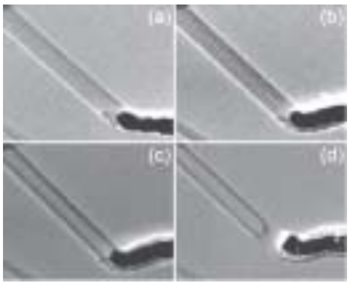

Fig. 2. An individual CNT under a current flow in the STM-TEM; (a-d) Consecutive steps of the tube shells and W electrode changes under passing current through the CNT/electrode interface.

(3) Making robust CNT circuits.

Multi-terminal CNT plumbing was performed under biasing and Joule heating of two (or more) crossed Co-particle filled CNTs (in-tandem with the convergent electron irradiation of the Co sites) using the STM-TEM specimen holder. Complex intra-diffusion processes resulted in transforming Co-filled CNTs into empty branched tubes tightly welded through a Co clamp (Fig. 3). Electrical transport and mechanical property measurements reveal high metallic conductivity and ultimate mechanical robustness of the junctions. The circuits possess resistances of only several tens kΩ and exhibit ultimately high tensile strengths of ~1-5 GPa.5,6)

Fig. 3. HRTEM image (left), structural model (center) and force- displacement curves (right) recorded under tensile loading of plumbed multi-walled CNTs inside the AFM-TEM holder.

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Nanostructured Metallic Materials

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1. Outline of Research

The purpose of this group is to obtain better understandings of structure-property relationships of various nanostructured materials as guiding principles to develop nanostructured materials with superior magnetic or mechanical properties for energy saving and data storage. The specific subjects in this group are: 1) development high coercivity magnets for hybrid electric vehicles by controlling interfacial nanostructure, 2) development of high density recording media for heat assisted recording (HAMR) and read sensors for next generaton hard disk drives (HDD) by the nanostructure control of magnetic thin films, and 3) development of high strength Mg alloys for weight reductions of transportation vehicles. Understanding the structure-property relationships of the above materials are essential to design and develop the materials with superior performances. However, because of their nanosized structure, characterizations of the structure and chemistry of these materials are becoming difficult despite the advances of modern nanostructure analytical techniques. To fill the gap between the required quantitative analylitical capability and the analytical limit of the TEM technique, we have been working on improving the performance of the 3D atom probe technique dramatically by employing short wave length femtosecond pulse lasers.

2. Research Activities

Recent successful implementation of pulse lasers to assist field evaporation have expanded the application areas of the 3D atom probe technique to a wide variety of materials including semiconductors and their thin film devices. Generally, it was believed that only electrical conductive materials can be analyzed by the atom probe technique. Although there have been a few successful analysis results of ultrathin film oxides like high-*k* films on Si or MgO in magnetic tunneling junctions, there have been no reports on successful atom probe analyses of bulk insulating ceramics. The main objective of this work was to demonstrate that even insulating bulk ceramics can be quantitatively analyzed by the 3DAP assisted with ultraviolent (UV) laser pulses 1). A Yb:KGW femtosecond laser with a third harmonic generator (λ=343 nm, 1.4 μJ/pulse, pulse duration of 400 fs) operating at the pulse frequency of 100 kHz was adopted to a locally built 3DAP instrument with CAMECA's fast delay line detector. As a demonstration sample, we have selected nanocomposite ceramics made of 3 mol% Y_2O_3 stabilized tetragonal ZrO_2 with 30mol% $MgAl_2O_4$ spinel. The average grain size of the t-ZrO_2 and $MgAl_2O_4$ were approximately 70 - 80 nm, respectively. The electrical resistivity of the sample was estimated at least 109 Ωcm. Even from such high resistivity material, we were able to observe field ion microscopy (FIM) images using Ne as an image gas. All the peaks of atom probe mass spectrum were attributed to the ions of all the constituent elements. Part of Al, Zr, and Y were detected as oxide molecular ions, and only Mg was detected as single atom ions without oxide molecular ions. The 3D reconstructed atom maps of Al+Mg, Y, Zr and O shows the presence of nanocrystalline Mg and Al rich grains ($MgAl_2O_4$) consistent with the microstructural feature observed by SEM and TEM. The atom probe tomography has also shown that Al and Y atoms were segregated along ZrO_2/ZrO_2 grain boundaries. We have further demonstrated that atom tomography can be obtained from Al_2O_3, MgO, $(Ce,Dy)O_2$, ZnO, Y_2O_3-ZrO_2 sintered bulk ceramics and other semiconductor devices. Based on these results, we will discuss the underlying mechanism of laser assisted field ionization of the atoms from nonconductive and high resistive materials.

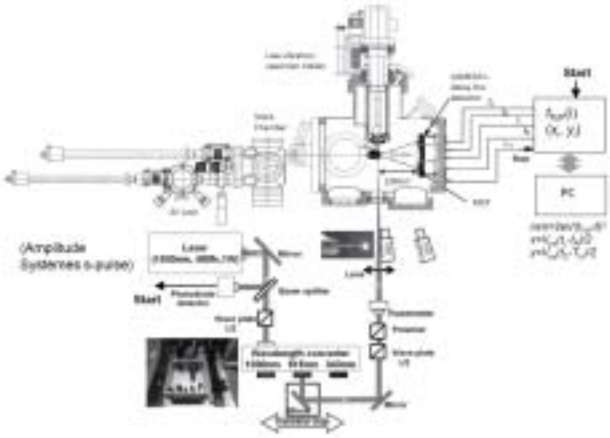

Fig. 1. Schematic of femotosecond laser assisted wide angle 3D atom probe.

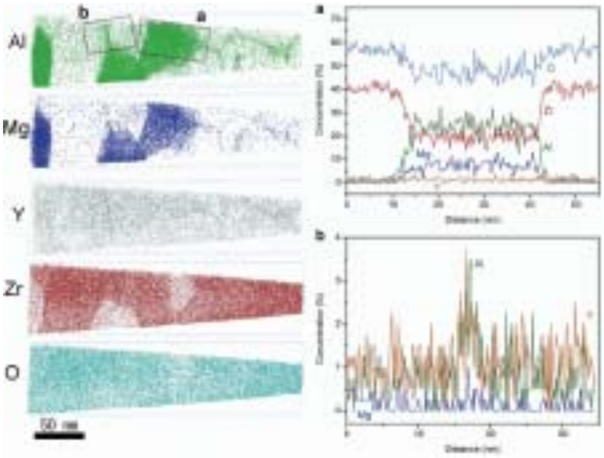

Fig. 2. 3D atom tomography of yittoria stabilized t-ZrO_2 and $MgAl_2O_4$ spinel nanocomposite. (a) and (b) show the concentration depth profiles obtained from subset volumes a and b.

Reference

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Photo-Ferroelectric Materials

MANA Principal Investigator **Kenji KITAMURA**
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1. Outline of Research

Lithium niobate ($LiNbO_3$) and tantalate ($LiTaO_3$) are typical ferroelectric materials possessing excellent piezoelectric, pyroelectric, opto-electric, photovoltaic and nonlinear optical properties. There is no material except them which has been studied and applied in so wide fields. As a nature of ferroelectric material, such effects depend on the direction of spontaneous polarization. When anti-parallel domains are created in a single crystal by locally inverting polarization, the patterned domain structures enable various new applications to be developed.

In order to promote efficiently collaborative research programs between NIMS and UW in interdisciplinary research fields, such as medical science, materials engineering, mechanical engineering, and aero-space science using such ferroelectric materials, .we have set up NIMS Overseas Operation Office at the University of Washing- ton. In this project, we are focusing on some research sub- themes using their photonic or photo-induced properties 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 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 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 are aiming to create novel multi-functions integrated templates using the surface potential patterns controlled by the external fields.

(3) ”Light induced pyroelectric effects for miniaturized X-ray generator”:

As the pyroelectric effect relies on a change in temperature, energy harvesting possibilities require temperature to vary in either space or time. Simplified models suggest that conversion efficiency depends on how quickly heating and cooling cycles are performed because the time scales for temperature change are typically much longer than for electronic interactions. Heat conduction through the crystal is the limiting step in the thermal exchange process, so in this study, we are focusing on the pyroelectric effect induced by the irradiation of a short pulse laser. A very small X-ray generation based on this pyroelectric effect using an electric heater is commercialized. However to miniaturize the generator and to deliver the ray to a small space, light-induced pyroelectrics will be necessary. This work is performed under the collaboration with UCLA.

2. Research Activities

(1) We have successfully demonstrated that a QPM device based on small, stoichiometric lithium tantalite single crystals can be used in the alternative laser surgery system with easily con-trolled temperature-tuning for multi-tissue ablation.

Fig. 1. Dental ablation of a human molar accomplished using 2.78 μm light from the novel QPM- based Tunable IR source. This crater diameter was measured to be 500 μm with a depth of 750 μm.

Fig. 2. Look down from the wall edge of the ablation crater in another molar tooth irradiated at 2.78 μm. No charring, burning, or collateral enamel degradation is apparent, only a smooth, even evisceration.

(2) We have demonstrated photoreduction of metal ions that resulted nano-metallic particles deposited on the polarized ferroelectric substrate. The metalized substrate can be applied for chemical or biochemical sensors by contact it with a solution of functional molecules having reactive groups that react with the deposited metal nanopartcles.

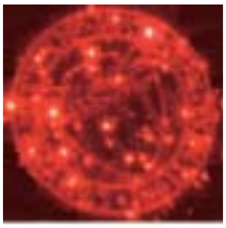

Fig. 3. Hibritaized DNA absorption on nano- mettalic particles deposited on patterned domain of LN template.

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Optoelectronic Materials

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MANA Research Associate Baoe Li, Yuhua Zhen, Jianyong Li

1. Outline of Research

For sustainable development of our society, energy harvesting (saving) and monitoring of environment are the most crucial issues. At this situation, development of materials for achieving high efficiency of power generation, low energy consumption of optoelectronic devices and high sensitivity of sensors are desirable. To this end, we devote ourselves to investigate structure-composition-property relationship in wide energy band gap materials to obtain new materials and structures appropriate for highly efficient devices and systems.

Our researches are categorized into following items.

(i) Synthesis of single crystalline materials and films, e.g., SnO_2, ZnO etc.
(ii) Fabrication of junctions, e.g., Au/$SrTiO_3$ etc.
(iii) Characterization of structures and evaluation of optoelectronic properties, e.g., electric rectification behavior and pulse response etc. .
(iv) Theoretical and experimental study on electronic structures, e.g., photoemission and DFT calculation.

Since we have basis of defect chemistry and solid state chemistry, these studies are carried out from the viewpoint of charge compensation in metal oxides.

2. Research Activities

(1) Electronic structure of oxide thin films[1,2,3].

For synthesis and application of nano-structures, we, absolutely, have to know if its properties are similar to the bulk ones or not. I n this viewpoint, we are comparing bulk and thin film properties of metal oxides. Particularly, we are interested in contribution of defect states and interfacial states of nano-structures to their properties. Although the thin films showed similar properties with bulk materials, e.g., similar electric conductivity, the electronic structure of thin films was sometimes obviously different from the bulk ones. For example, Fig. 1 shows a result of Fourier-transformed DLTS for ZnO thin films.[4] This result suggests that there are, at least, three energy levels within the bandgap of this sample. Moreover, concentration of an energy level, E3, was considerably higher than ordinary bulk ZnO (not shown). Namely, nature of defects in nano-sized structures was different from that for bulk. Since the nano-sized materials are synthesized at relatively low temperature in comparison to bulk materials, presence of some non-relaxed structures due to low temperature synthesis are likely the origins of such defect structures.

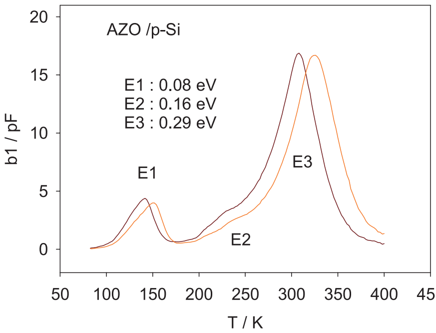

Fig. 1. Transient capacitance measurement for ZnO thin films for transparent electrode applications.

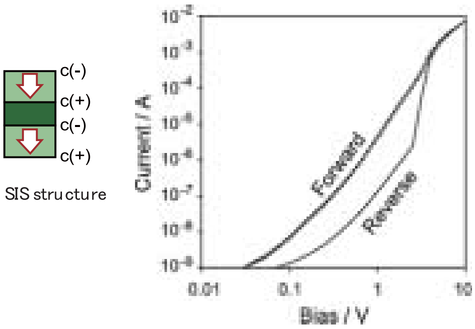

Fig. 2. Asymmetric *I-V* behavior observed at SIS structure interface composed of polar ZnO crystals as also shown.

(2) Polarity in semiconductors[5,6,7]

Since many wide energy band gap semiconductors show crystalline polarity due to absence of inversion symmetry in their crystal structure, effect of polarity, such as pyroelectricity and piezoelectricity, on performance of semiconductor devices is of great importance for further development of materials and devices. Thus, we are investigating atomic arrangement at the hetero-structures composed of polar semiconductors and the effect of the polarity on electronic structures and interfacial properties of those hetero-interfaces. For example, semiconductor/insulator/semiconductor (SIS) interface made from polar ZnO crystal and oxide glass insulator showed asymmetric or symmetric I-V and C-V behavior depending on the polarity of ZnO (Fig. 2). The origin of such asymmetry is under investigation in terms of the influence of crystalline polarity on formation of interfacial state.

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Structure Controlled Ceramics

MANA Principal Investigator **Yoshio SAKKA**
MANA Research Associate Chunfen Hu, Weihua Di
Graduate Student Salvatore Grasso, Mamiko Kawakita, Wang Lin

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 stimulation 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) has 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 extremely 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.

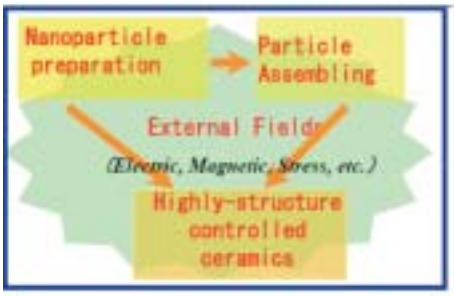

Fig. 1. Three sub-themes and their organic coordination for conducting effective materials exploration research.

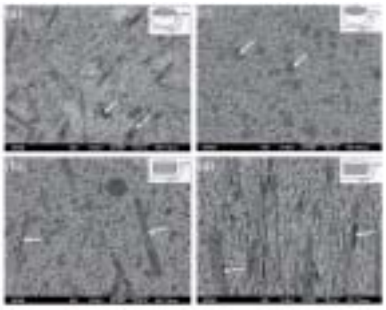

Fig. 2. SEM photos of sintered samples prepared by slip casting in the rotational magnetic field of 1 T (a) (b) and 12 T (c) and (d).

2. Research Activities

(1) The c-axis texturing of Si_3N_4 by slip casting in a rotating magnetic field [1)]

The c-axis texture development in seeded Si_3N_4 with β-Si_3N_4 whiskers by slip casting in a rotating magnetic field was investigated by increasing the magnetic flux density from 1 to 12 T. The resultant c-axis textured Si_3N_4 (Fig. 2) exhibits thermal anisotropy as high as 55%, slightly lower than the intrinsic thermal anisotropy (62%) of β-Si_3N_4. A theoretical analysis is performed to help understand the key factors affecting the orientation of β-Si_3N_4 whiskers.

Fig. 3. Scheme of the proposed methodology based on SPS current control mode (CCm) experiments and simulations.

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

The developed SPS model used a moving-mesh technique to account for the electrothermal contact resistance change during both shrinkage and punch sliding follow-up.(Fig. 3) The experimental and numerical results showed the effects of pressure on grain growth, residual porosity, and hardness observed along the sample radius. Upon increasing sintering pressure, complete densification was obtained by reducing the peak temperature measured at the die surface. By combining experimental and modeling results, a direct correlation between compact microstructure homogeneity and sintering parameters (i.e., temperature and applied pressure) was established.

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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 T_c 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.

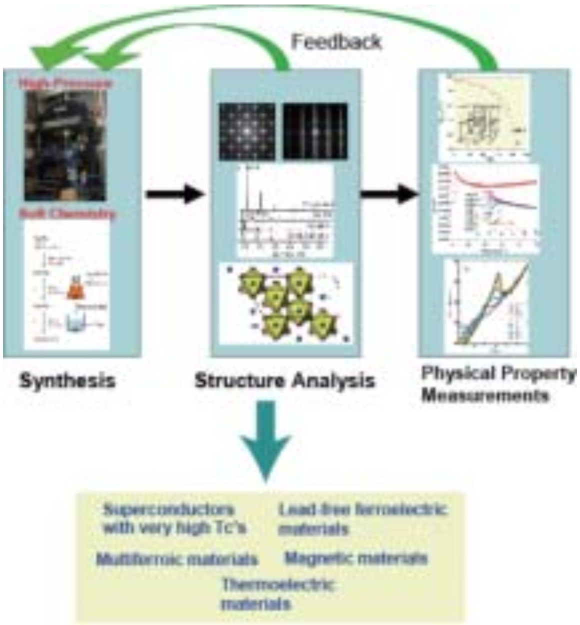

Fig. 1. Three sub-themes and their organic coordination for conducting effective materials exploration research.

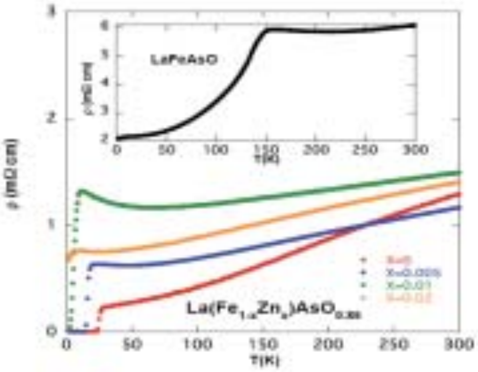

Fig. 2. Temperature dependence of electrical resistivity for $LaFe_{1-x}Zn_xAsO_{0.85}$.

2. Research Activities

(1) *Drastic suppression of superconductivity by Zn substitution in* $LaFe_{1-x}Zn_xAsO_{0.85}$ [1)]

$LaFe_{1-x}Zn_xAsO_{0.85}$ (x=0-0.03; T_c = 26 K for the Zn-free compound) was prepared using the high-pressure technique. Bulk superconductivity was suppressed almost completely by no more than 3 at.% of the Zn atoms at the Fe sites. Such drastic suppression by the nonmagnetic impurity has been theoretically predicted for the s_{+-} wave model, a promising mechanism for the Fe pnictide superconductors. The present result attracts attention widely as the compelling experimental evidence supporting the s_{+-} pairing mechanism.

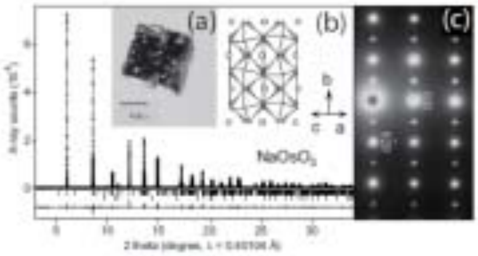

Fig. 3. Single crystal and Rietveld analysis of $NaOsO_3$.

(2) *Continuous metal-insulator transition of the antiferromagnetic perovskite* $NaOsO_3$ [2)]

The perovskite $NaOsO_3$ was prepared under high pressure. This compound was found to have quite interesting physical properties; it shows a Curie-Weiss metallic nature at high temperature and suddenly goes into an antiferromagnetically insulating state at 410 K on cooling. Electronic specific heat at the low-temperature limit is absent, indicating that the band gap fully opens. It is most likely that the antiferromagnetic correlation plays an essential role in the gap opening.

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Photonic Structures in Nature

MANA Principal Investigator **Zhong Lin WANG**
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Research Scientist Yong Ding
Graduate Student Sheng Xu

1. Outline of Research

Photonic crystals (PCs) are one of the most active research fields today. They are a class of materials or structures in which the dielectric function or refraction index experiences a spatially periodic variation. In nature, tremendous numbers of living creatures, for example, some butterflies, beetles and peacock, exhibit striking brilliancy colors. Most of their colors, also named as structural colors, do not come from the pigments, but from their periodic nature-made PCs, or biophotonic materials. Such biologically self-assembled PCs are ideal examples, which can inspire us in design and fabrication of new photonic structures, and also can serve directly as bio-templates to mimic those structures.

Our work in the passed year was focused on the understanding of the structural origin of the brilliant colors from both the cover and ground *Morpho Peleides* butterfly scales.

2. Research Activities

The different orientation-dependent structure colors from cover and ground scales of *Morpho Peleides* butterfly can be revealed in Fig. 1.

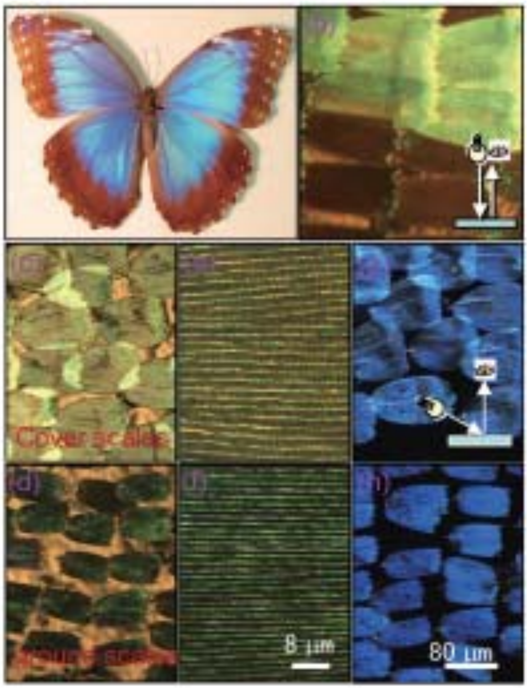
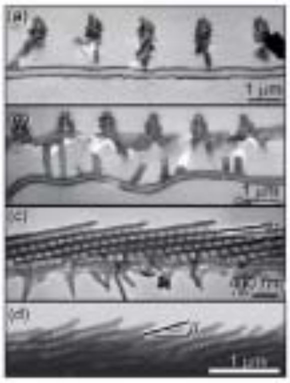


Fig. 1. **(a) An optical photo of a male Morpho Peleides butterfly. (b) An optical microscopy image of the scales on the wing at normal incidence. (c), (e) and (d), (f) Low and high magnification optical images of the cover and ground scales, respectively, when illuminated in the normal direction. (g) and (h) Optical images of the cover and ground scales, respectively, when illuminated from the side as schematically shown in (g). The scales change colors with the change of illuminating direction.**

The structure differences between the cover and ground scales can be revealed in the cross-section transmission electron microscopy (TEM) images as shown in Fig. 2. Figure 3 (a), (b) and (c) gives the reflection spectra from wing, pure cover scales and pure ground scales, respectively.



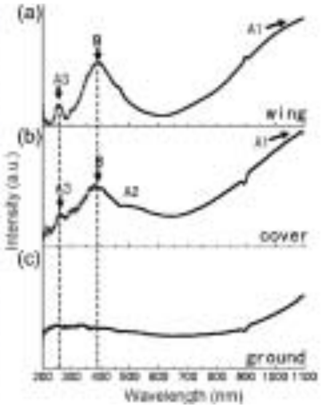


Fig. 2. **(left) Cross-section TEM images of the cover (a), (c) and ground (b), (d) scales viewing along and perpendicular to the ridges, respectively. The samples used for TEM imaging were coated with a thin layer of alumina by ALD. The inclination angles α and β of the shelf to scale surface in cover and ground scales are close to 7° and 17°, respectively.**

Fig. 3. **(right) Reflection spectra of the original wing (a), pure cover (b), pure ground scales (c) with incidence angle as 33° from the tail direction. The tiny peaks and bumps at 466 nm and 896 nm are from the measurement system.**

In reflection spectra, there have totally four peaks, assigned as A1, A2, A3 and B, been identified. The blue color related peak B is mainly contributed by the Bragg reflection from the shelf structure in the scale ridges. The A1, A2 and A3 peaks come from the thin film interference effect of the base plate. Due to the different inclination angles of the shelves relative to their scale planes, the beams with the same incidence angle will be reflected to different directions by the cover and ground scales. The missing of A1, A2 and A3 reflection peaks in the ground scales is due to the densely arranged cross-ribs and trabeculae on the scale, which screen the thin film interference effect contributed by its base plate.

Our study has provided a detailed interpretation regarding the nature of the reflections peaks in the reflection spectra from the butterfly wing. Such an understanding gives us an opportunity to deliberately modify the structure of a particular structural component using nanofabrication techniques, so that unique optical properties can be tuned. This is a direction towards smart biophotonics that is composed of smart and functional materials, which are responsive to the environment such as electric field, humidity and gases.

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Nano-System Architectonics

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MANA Research Associate Hiromi Kuramochi, Hiroyuki Tomimoto, Liu Kewei, Swapan K. Mandal, Keita Mitsui

1. Outline of Research

The goal of our Nano-System Construction Group is to create new nano-systems with novel functionality by the use of various key technologies for "materials nanoarchitectonics" and put the created nano-systems to practical use to contribute to our society in such forms as next-generation information processing and communica- tion, environmental and energy sustainability, and regenerative medicine.

To achieve this interdisciplinary research, we make close collaboration with other groups in MANA as shown in Fig.1. We are also making collaboration with MANA's satellite labs headed by Prof. Jim Gimzewski (UCLA, USA), Prof. Mark Welland (Univ. of Cambridge, UK), Prof. Christian Joachim (CNRS, France).

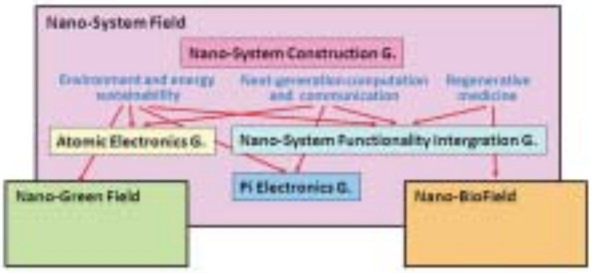

Fig. 1. Collaborationof the Nano-System Construction Group with other groups in MANA.

2. Research Activities

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

1) Electrically wiring single functional molecules by the use of conductive polymer wires.
2) Development and application of a novel scanning-probe method to measure nanomagnetism using non-magnetic probe.
3) Atomic switch: 1) Practical use (commercialization) 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 (polydi- acetylene)[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 nanowiring (see STM images in Figs. 2c and d).

We have developed a new scanning-probe method to measure nanomagnetism using no magnetip tip5), 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.

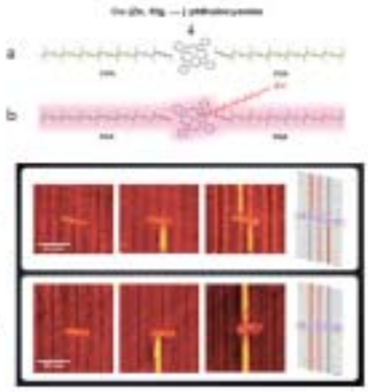

Fig. 2. Wiring a single phthalocyanine molecule with conductive polydiacetylene molecular chains. Schematic figures (a, b) and STM images (c, d).

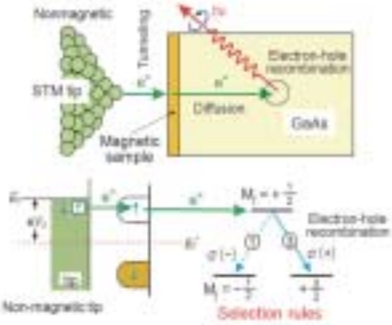

Fig. 3. Principle of a developed novel method to measure nano-magnetism conveniently.

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Extreme-Field Nanofunctionality

MANA Principal Investigator **Daisuke FUJITA**
MANA Research Associate Jian-Hua Gao, Hongxuan Guo

1. Outline of Research

In the nanoscale world on solid surface, where dimensionality is limited to two, one and zero, low-dimensional functionality may appear. Such a novel nanofunctionality can lead us to innovation towards new nanoscale systems. Most of nanoscale functionality stems from quantum mechanical effects in addition to size and surface effects. Generally, its remarkable appearance is expected in extreme environments such as low temperature, high magnetic field, and ultrahigh vacuum, where the control of field parameters plays an important role. Moreover, the combination of surfaces and controlled environments may cause low-dimensional phases through a wide range of self organizations such as adsorption, segregation, reconstruction, precipitation and so on. Spontaneous phase transition is possible by giving a perturbation with nanoscale probes. Thus, the research composed of self organization, extreme environments and nano probes is our main theme. The purposes of research are creation of novel surface nanoscale systems, and exploration of novel nanofunctionality using advanced nanoprobe technology (Fig. 1).

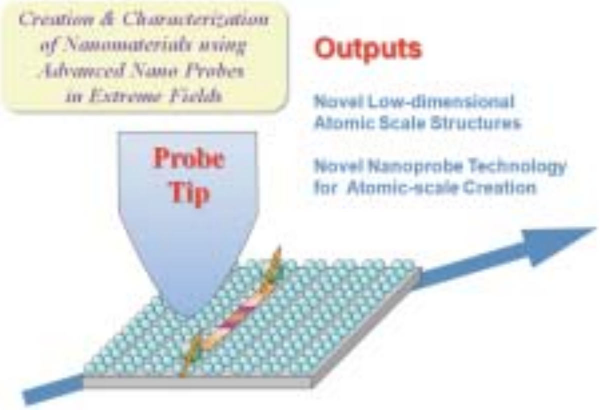

Fig. 1. Schematic of research methodology and possible outputs.

2. Research Activities

(1) Silicon adatom switching and manipulation on Si(111)-7×7 Surface[1)]

At low-temperature and in ultrahigh vacuum (UHV) environment, a multiple-state switching behavior in the tip height or tunneling current of scanning tunneling microscopy (STM) has been found on Si(111)-7×7 surface. This novel switching is caused by displacement of silicon adatoms under the influence of energetic tunneling electrons (Fig.2). When the tip is fixed over a center adatom, five well-defined levels appear in the measured tip height and tunneling current. These levels are attributed to different electronic structures, depending on the configuration of the center adatoms in the unit cell. We also demonstrate manipulations of the center adatoms by controlling the sample bias.

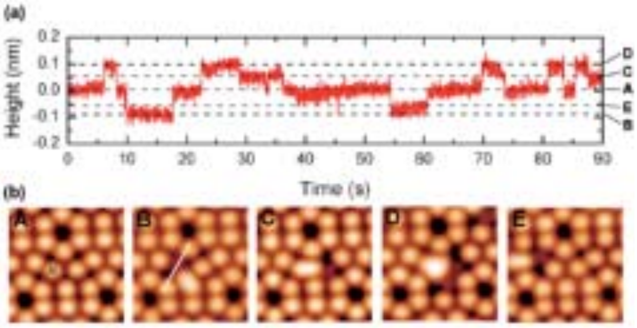

Fig. 2. (a) Tip height as a function of time. (b) STM images for different height levels emerged in (a).

(2) Unique Synthesis of Few-layer Graphene Films

Graphene is a single layer of 2-D carbon atoms arranged into honeycomb lattice. Intensive research has been initiated due to its high carrier mobility, chemical inertness, excellent thermal conductivity and so forth. Using surface segregation and 3-D precipitation processes, we have developed a unique synthesis method for graphene films on various carbon-doped metal surfaces[2)]. For example, on a C-doped Pt(111) surface, growth of few-layer graphene and carbon nanowire has been confirmed by Atomic Force Microscope (AFM) and Auger Electron Spectroscopy (AES). Discrete contrast observed in Auger mapping corresponds to different layer number of graphene films (Fig. 3). Furthermore, the growth of carbon nanowires has been evidenced by AFM and STM characterization.

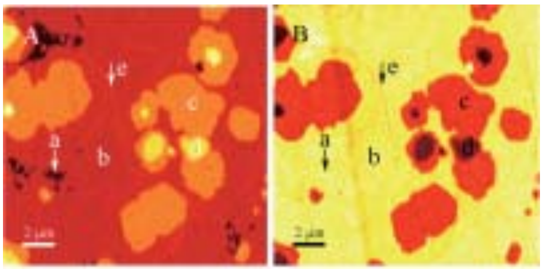

Fig. 3. Auger mapping of C KLL (A) and Pt(NOO) (B) of graphene films on Pt(111) surfaces. Area a: Pt(111) with segregated carbon atoms; area b, c, d correspond to monolayer, bilayer and trilayer graphene; area e is carbon nanowire.

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MANA Brain: Atomic Neural Networks

MANA Principal Investigator **James K. GIMZEWSKI**
(Satellite at UCLA, USA)
Technical Director Adam Z. Stieg
MANA Post-doc Greg Pawin
Graduate Student Cristina Martin-Olmos, Haider Rasool

1. Outline of Research

Future development in computational systems will be fundamentally limited by a variety of factors, including but not limited to: the speed of light, thermal and electrical coupling, fundamental quantum mechanics, entropy and the Von Neumann bottle neck between processing and memory. We are developing a novel hardware-based, physically intelligent neural network through a synergy of biological inspiration and advanced nano-electroionics using the exciting properties of atomic-switch technology. In contrast to traditional approaches of neural network design that employ open circuit architectures and software design/ implementation, we seek to demonstrate the first human-engineered open thermodynamic systems that spontaneously evolve non-trivial "intelligent" behavior

through advanced applications of atomic switching technology in dynamic nanowire networks.

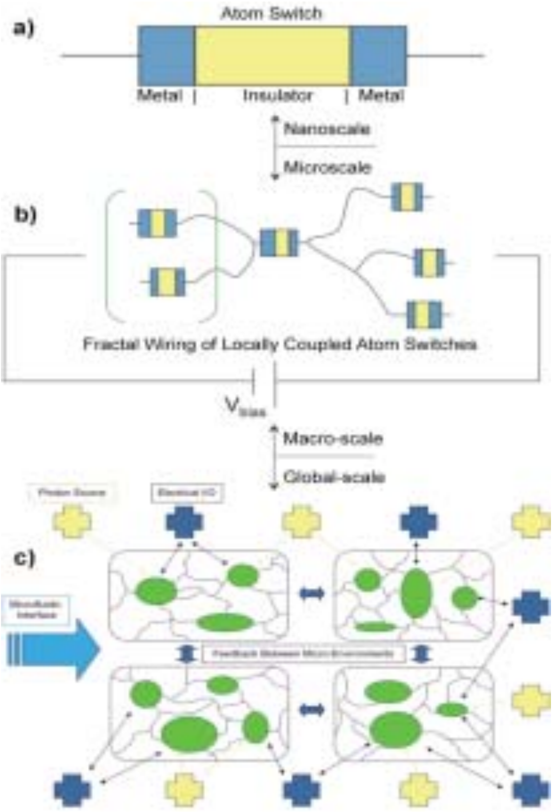

Figure 1. **Clusters of coupled switches (represented in green) wire together dendritically to form individually addressable, micro-scale environments which are further connected by wires and fluid flow into a global neuromorphic architecture.**

2. Research Activities

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

1. Fabrication of two-dimensional atom-switch networks though solution phase self-assembly
2. Examination of memristive device characteristics
3. Exploration of coupling and network effects within and between switching arrays

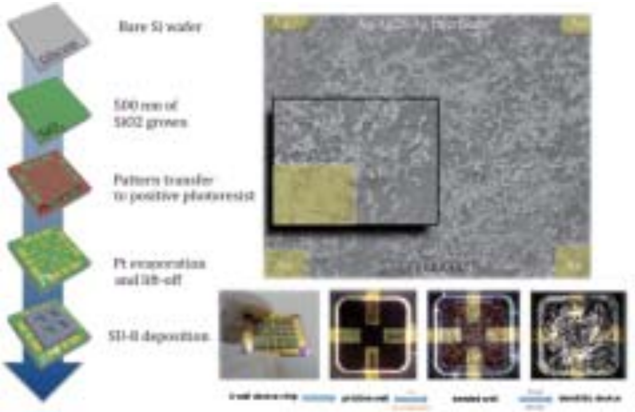

Figure 2. **Fabrication scheme, scanning electron micrograph and optical image of four-terminal dendritic network switching device.**

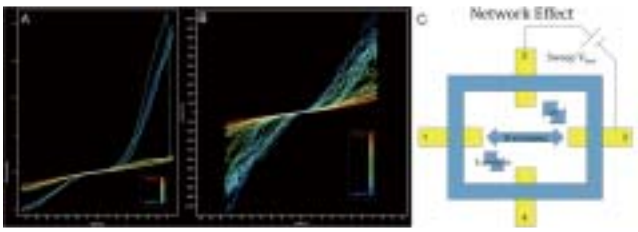

Figure 3. **Representative electrical characteristics of dendritic device networks demonstrating hysteretic, memristive and network behaviors.**

Future work will involve optimization of fabrication methods, the development of 3D architectures, further elucidation of intra- and inter-network coupling mechanisms, and the introduction of a dynamic solution environment.

Recent Publications with MANA recognition:

T. Hasegawa, K. Terabe, T. Tsuruoka, T. Nakayama, J.K. Gimzewski and M. Aono *In Press:* Advanced Materials (2009).

A.Z Stieg and J.K Gimzewski *"Local Probes: Pushing the limits of detection and interaction" In Press:* Handbook of Nanophysics (2009).

H.I Rasool, P.R. Wilkinson, A.Z. Stieg and J.K. Gimzewski *In Press:* Review of Scientific Instruments (2009).

Atomic Electronics for Future Computing

MANA Principal Investigator **Tsuyoshi HASEGAWA**
MANA Scientist Kazuya Terabe, Tohru Tsuruoka
MANA Research Associate Takeo Ohno, Shouming Wu, Alpana Nayak

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 conceptually new logic systems, which changes by itself according to the logical operation. We believe that neural computing systems are ultimate style of the non-volatile logic systems.

In order to accomplish the purpose, we will conduct 1) basic research on nanoionic 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.

2. Research Activities

(1) Development of Organic Atomic Switch[1)]

Organic devices are required to develop flexible electronic devices such as used in ubiquitous computing. Though there is an organic field effect transistor as a logic device, there is no promising memory device. Since the atomic switch consisting of inorganic materials such as Ta_2O_5 is in the final stage for commercialization, an organic atomic switch will be a promising flexible memory device.

We developed an organic atomic switch using silver-doped polyethylene oxide (PEO) as an ionic conductive material. The fabricated organic atomic switch shows switching properties similar to that of inorganic atomic switches. Namely, it shows bipolar switching as shown in Fig. 1. Cyclic endurance of 10^6 times and retention time of one week have been achieved using the prototype. Cycled read-write-erase-read operation using pulsed bias voltages was also achieved.

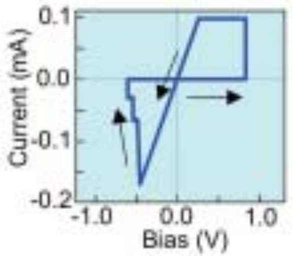

Fig. 1. Switching property of the organic atomic switch made of silver-doped polyethylene oxide.

(2) Demonstration of Learning Abilities using Ag_2S Atomic Switches[2)]

We have demonstrated learning abilities using Ag_2S atomic switches. Short-term memory (STM) and long-term memory (LTM) are realized by utilizing the two modes of atomic switch electron flows, i.e., tunneling mode and ballistic mode. Neuroplasticity was also demonstrated as shown in Fig. 2, where the atomic switch can store the information of input signals till it 'fires'. The characteristics have potential for developing all solid-state neural computing systems.

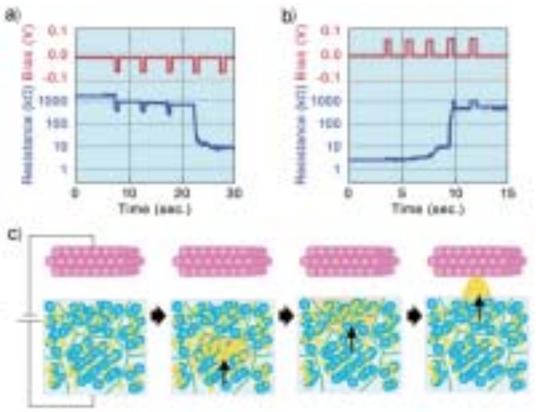

Fig. 2. Experimental results showing a neuroplasticity. a) Turning on and b) turning off processes. c) Operating mechanism for the turning on processes is schematically shown.

(3) Fundamental Researches

We have investigated temperature and bias dependences of atomic switching, and revealed the rate-limiting processes in the atomic switch operation.[3)] We also succeeded in measuring I/V characteristics of atomic scale nanostructures which was predicted to be conductive.[4)]

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Nano Superconductivity and Terahertz Emission

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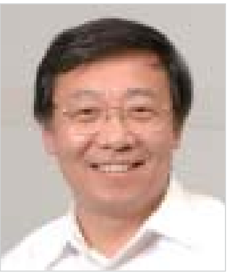
Graduate Student	Shi-Zeng Lin



1. Outline of Research

Terahertz (10^{12}Hertz, THz) electromagnetic (EM) waves are useful in many applications such as DNA diagnosis, observation on ultrafast dynamics of electrons in materials, telecommunication, and so on. However, development of strong and compact source of THz waves is still very challenging.

Josephson effects are associated with the quantum tunneling of Cooper pairs across the superconductor/insulator/superconductor structure, called Josephson junction, which induce Josephson plasma, a composite wave of superconductivity phase and EM oscillation. Based on this principle, a research team of Argonne National Lab of US and University of Tsukuba of Japan succeeded in stimulating strong monochromatic EM wave from a mesa structure of single crystal of $Bi_2Sr_2CaCu_2O_8$, a typical cuprate high-Tc superconductor.

This layered superconductor behaves in many aspects like a sequence of Josephson junctions stacked along its c axis with huge inductive coupling between neighboring junctions, since the stacking period is as small as 1.5 nanometers. Analyzing the coupled sine-Gordon equations as the mathematical model of the material, we have discovered a novel state for the superconductivity phase dynamics. Under the dc voltage bias, the system develops a π phase twist inside each junction when superconductivity phases are rotating overall, which provides a strong coupling between the standing wave of Josephson plasma and the driving current. When the bias voltage is tuned appropriately, a cavity resonance in the mesa of single crystal takes place with the amplitude of Josephson plasma enhanced greatly, which results in large dc current injection into the system and strong radiation of THz waves from the edge.

In order to reduce the energy cost of the π phase twist, the system piles up + and – π phase kinks alternatively in the stacking direction, which corresponds to one of the eigenvectors of the coupling matrix of the coupled sine-Gordon equations. The attractive interaction between the opposite π kinks makes the π kink state stable.

Our theory provides a consistent explanation on the experimental observations, and predicts that the optimal radiation power is larger than the observed value by orders of magnitude. These results reveal the possibility of a novel quantum source of EM wave based on a principle totally different from the conventional laser.

2. Research Activities

(1) Josephson plasma and THz radiation in a cylindrical mesa of cuprate high-Tc superconductor[1,2]

In order to reveal the shape of standing wave of Josephson plasma inside the cavity formed by the superconductor mesa, we propose to use cylinder geometry instead of the rectangle one used in the first experiment. The radius dependence of the radiation frequency observed in a recent experiment indicates clearly that the tangential component of magnetic field of the Josephson plasma is zero at the perimeter of the mesa (Fig.1), as addressed in our theory. These research activities improve much the understanding on the cavity resonance of Josephson plasma and the strong THz radiation.

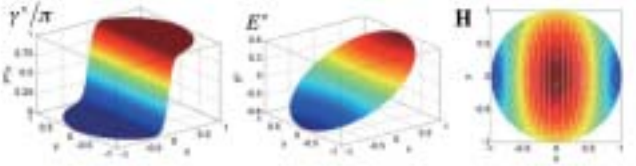


Fig. 1. **π phase kink of the superconductivity phase in a cylindrical mesa of the cuprate superconductor BSCCO-2212 and the electric and magnetic field of the standing wave of Josephson plasma.**

(2) Identification of dynamically dominant excitations in antiferromagnetic chains in a magnetic field[3]

Using exact Bethe-ansatz solutions, we investigated dynamical properties of the spin-1/2 antiferromagnetic Heisenberg chain in a magnetic field (Fig.2). In particular, we found that the 2-string solutions in the Bethe ansatz carry large spectral weights in the high-energy regime. The continuum originating from the 2-string solutions naturally explains puzzling experimental results observed in one-dimensional antiferromagnets in a magnetic field.

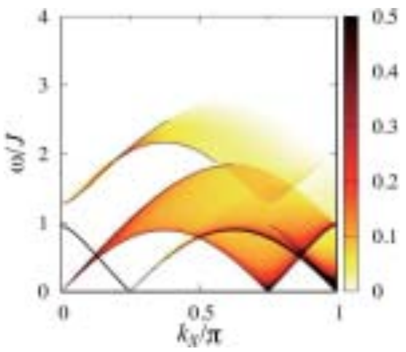


Fig. 2. **Dynamical structure factor S(k,ω) in the spin-1/2 antiferromagnetic Heisenberg chain in a magnetic field.**

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Surface Atomic Scale Logic Gate

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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 to assemble a nano-system which will be able to perform by itself a complex 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 to understand the physics of surface interconnection of simple single molecule logic gate (or surface atomic circuit logic gate) using atomic wire, 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

(1) Surface atomic scale logic gate

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. Two passivated semiconductor surfaces are of interest for the Toulouse MANA Satellite: MoS2 and Si(100)H. For MoS2, the single S atom extraction was studied in NIMS in collaboration with the MANA satellite in Toulouse 1). For Si(100)H, we have first preferred to study a realistic implantation of a classical molecule OR gate (Fig.1). The goal is to determine the exact chemical structure of the molecule OR contacted by surface atomic wires on Si(100)H and to determine the best solution between a complete surface atomic wire circuit and an hybrid solution with a molecule interconnected by surface atomic wires 2).

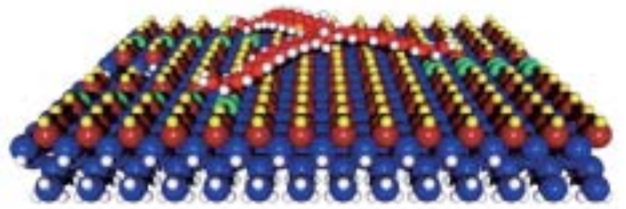

Fig. 1. A possible surface implantation of a classical molecule starphene like OR logic gate interconnected using surface dangling bond atomic wires.

For a qubit approach of single molecule logic gates, a complete SWAP 4 centers mixed valence complex molecule was designed 3) and its chemical synthesis started 4). The originality of the SWAP molecule Fig. 2 relies on the optical control of the swapping operation using a through bond electron transfer process able to disentangle the 2 swapping qubits of this molecule.

Fig. 2. The chemical structure of a 2 qubits swap molecule under chemical synthesis in the Toulouse MANA satellite surface implantation of a classical molecule starphene like OR logic gate interconnected using surface dangling bond atomic wires.

For a Quantum Hamiltonian Computing (QHC) molecule logic gate approach 5), a symbolic analysis for complex logic gate was fully developed 5) and applied to the construction of tight binding matrices up to the 2 x 2 full adder whose minimum quantum Hamiltonian is a 31 x 31 matrix. This model was very useful to interpret the logic operation of a simple QHC molecule logic gate. It was also extended to surface atomic logic gate to be constructed on Si(100)H where each fabricated surface dangling bond must be represented by a 5 x 5 matrix hamiltonian leading to a fantastic quantum control problem for the design of an Si(100)H dangling bond surface logic gate.

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Superconducting Quantum Nanoarchitectonics

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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 by making use of modern nanotechnology in the ultimate quantum regime of materials. The challenge to pursue this on the nature of the intrinsic Josephson junctions (IJJs) with and without magnetic field has been set forth using high-T_c superconductor (HTSC) $Bi_2Sr_2CaCu_2O_{8+\delta}$, which can be grown by us in the 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 electromagnetic waves at THz frequencies were observed and the spectrum was analyzed by a spectrometer. This achievement has attracted much attention because this technology may bring us the first full solid state THz sources, which are ideal and desired for a variety of important applications in the 21st century.

2. Research Activities

(1) THz radiation from HTSC IJJs

In order to better understand the mechanism of THz radiation from IJJs, we have performed the measurement of spatial variation of the radiation intensity emitted from various shapes and dimensions of the mesa. Figure 1and 2 show the examples of them around the rectangular mesa (60 μm x 400 μm x 1.2 μm) rotated around y- and z-axes, respectively. The intensity has a characteristic peak at about ± 30° from the top, where a shallow minimum was found. It turns out that this dip feature cannot be explained simply by the cavity resonance mode used by Koshelev, and Hu and Lin, *et al.*, and leads to introduce a uniform Josephson current contribution for the radiation[4]. The solid curves shown in Figs. 1 and 2 mean the fits to the two radiation source model[4], and they agree well with experimental results. Neither only cavity resonance model nor simply uniform Josephson current is sufficient as seen in the dashed curves in Fig. 1 and 2. The electromagnetic wave excited in the mesa is identified to be the TM(0,1) mode, not the TM(1,0) mode, which is expected from the cavity resonance model used and the conventional patch antenna theory. This peculiarity seems to originate from the fact that the plasma frequency $\omega_p = c_0/\varepsilon^{1/2}\lambda_c$ sets a lower limitation to the propagation of EM waves in the mesa.

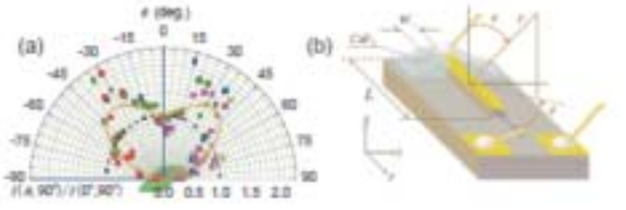

Fig. 1. (a): The spatial distribution of the radiation intensity from the rectangular mesa shown in (b).

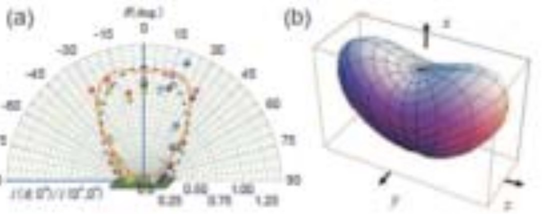

Fig. 2. (a) The spatial distribution of radiation rotated around z-axis. (b): All around spatial distribution of radiation obtained from the two source model[4].

(2) Search for novel superconductors

Development of the novel superconducting materials is needed for pursuing the superconducting quantum nanoarchitectonics. Here, we show an example of a successful growth of high quality single crystal of $BaFe_2(As_{1-x}P_x)_2$ compound as shown in Fig. 3, where the electrical resistivity is given. It exhibits a remarkable linear behavior from room temperature down to T_c=31 K at the optimal P concentration with x=0.30 (d$\rho(T)$/dT=0.57 μΩcm/K). The sharp superconducting transition, the *RRR* ratio exceeding 10, and the extrapolated residual resistance of 3 μΩcm indicate high quality single crystal (a photograph is shown in Fig. 3) to be measured thoroughly.

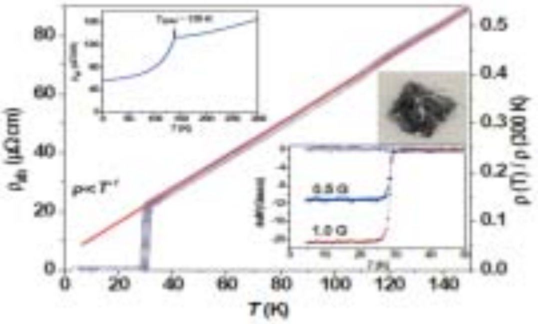

Fig. 3. A remarkable linear temperature dependence of the *ab*-plane resistivity observed in $BaFe_2(As_{1-x}P_x)_2$ single crystal with x=0 (upper left) and 0.32(main). Diamagnetism below T_c is also given (lower right).

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Integration of Nano Functionality for Novel Nanosystems

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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 (MSPM), 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.

MSPM 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 MSPM and related techniques to understand the signal transfer from nanoscopic viewpoints.

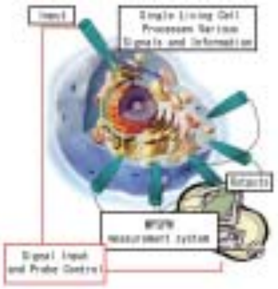

Fig.1. Schematic illustration of a "cell odyssey" using the MSPM which works in liquid environment.

2. Research Activities

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

Our MSPM 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. Examples of such measurements of single nanowires have been done for $ErSi_2$ on Si(001)[4)], Pt silicide on Si(001)[5)] and CNTs.

(2) Controlling reversible intermolecular reaction for data storage[8,9)]

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. 2, this control can be done reversibly thus applied for future data storage with a bit density of 190 Tbits/in^2.

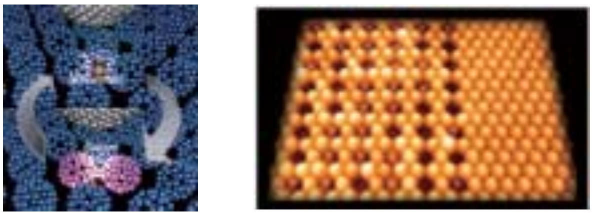

Fig. 2. Left panel: Schematic illustration of intermolecular chemical reaction controlled by STM. Right panel: Array of single-molecule-level bits recorded in a thin film of C60 using the controlled intermolecular reaction.

(3) Application of MSPM to living nerve cells[10,11)].

To understand the signal processing scheme used by the brain, we developed nanoprobes which can be used in liquid and inserted into living cells10,11). Combination of such nanoprobes and MSPM enables "cell odyssey" using MSPM.

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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.

(1) Nano-SQUID

We are now developing 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 and spins in dots (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.

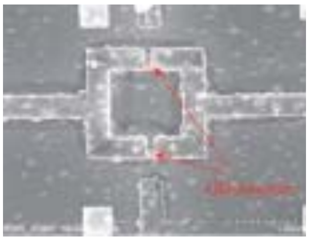

Fig. 1. Nano-SQUID with embedded quantum dots.

(2) Superconductor-based LED

We are also working on superconductor-based Light Emitting Diode (Fig. 2). Superconductor-based LED is expected to be the key device in quantum information technology because of its promising giant oscillator strength due to the large coherence volume of the superconducting pairs together with the possibility of the *on-demand* generation of entangled photon pairs. The enhancement of the electroluminescence in the active layer accompanying the superconducting transition of the electrode is demonstrated [1], and theoretical understanding is established [2].

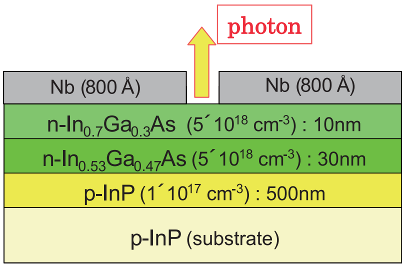

Fig. 2. Schematic cross sectional view of the superconductor-based LED.

2. Research Activities

(1) Discovery of Josephson effect in a superconducting-based LED [3]

We confirmed Josephson effect between two superconducting electrodes at the *n*-type semiconductor side of a superconductor-based LED (Fig. 3). The characteristics of the Josephson junction are found to be modulated by applying voltage to the normal electrode at the *p*-type semiconductor side. The Josephson junction characteristics show an extraordinary sensitivity to the radiative recombination process, that we estimate as the recombination efficiency. This work was done in collaboration with Hokkaido Univ., NTT and Hamamatsu Photonics.

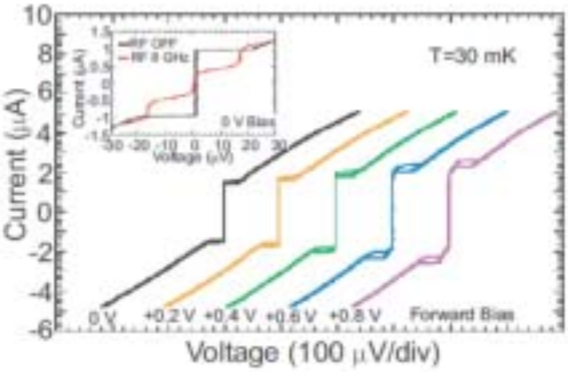

Fig. 3. Current-voltage characteristics of the Nb/n-InGaAs /Nb junction on the LED surface measured at 30 mK. A clear supercurrent is observed. The inset data measured with 8 GHz microwave irradiation shows ac Josephson effect.

(2) Readout process of a flux qubit by a Josepshon bifurcation amplifier [4]

We analyzed the Josephson bifurcation amplifier (JBA) readout process of a superconducting qubit quantum mechanically by calculating the dynamics of the density operator of a driven nonlinear oscillator and a qubit coupled system during the measurement process. From the analysis results, we have succeeded in extracting the essential feature of the JBA readout process of a superconducting qubit. This work was done in collaboration with NTT BRL.

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Gate-Induced Band Gap in Bilayer Graphene

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1. Outline of Research

A band gap formation in graphene is one of the most important key challenges for graphene switching device. The graphene device is expected to potentially realize future high performance nanoscale electronics. One of the advantages of graphene over conventional semiconductor is that the graphene is conductive even without doping; the uncertainty in the dopant position limits further miniaturization of conventional silicon transistors. As another merit, atomic thickness is realized in self-organized channel. Graphene has other merits, including high mobility, low contact resistance with metal electrodes, feasibility of nanoscale fabrication, and resource abundance. For application to transistors, opening a wide band gap is required to shut off a current in the off-state.

We experimentally investigated the transport properties of bilayer graphene gated by top and back gate. Highly doped Si substrate was used as the back gate, and originally developed Al-electrode evaporated on the graphene was used as the top gate [1]. 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 p-electron electronics.

2. Research Activities

An ambipolar resistance peak observed at the transition between the p-type and the n-type conduction in the grapheme was enhanced as the high electric field between the dual gates was increased. It was found that the resistance enhancement was only observed in bilayer grapheme while the mono-, tri-, and tetralayer graphene never showed the clear enhancement.

In a conductance plot of the ambipolar behaviour in a top-gate voltage scan, when the resistance was enhanced in the electric field, the conductance closely approached zero conduction. Voltage difference extracted from the threshold of the p-type and the n-type region in the top-gate voltage scan was typically 0.5 V at the gate electric field of 1.4 V/nm, and strongly depended on the applied electric field. The threshold region would imply an existence of the band gap when the electric field was applied.

As a further experiment, temperature dependence of the ambipolar resistance peak was carried out. The conductance extracted from the peak resistance was well fitted by thermal activations with two conduction components. One of them was based on the conduction due to the variable range hopping conduction via localized states [2]. Another component was caused with the larger activation energy over 100 meV, suggesting the existence of the band gap in the order of hundreds of meV.

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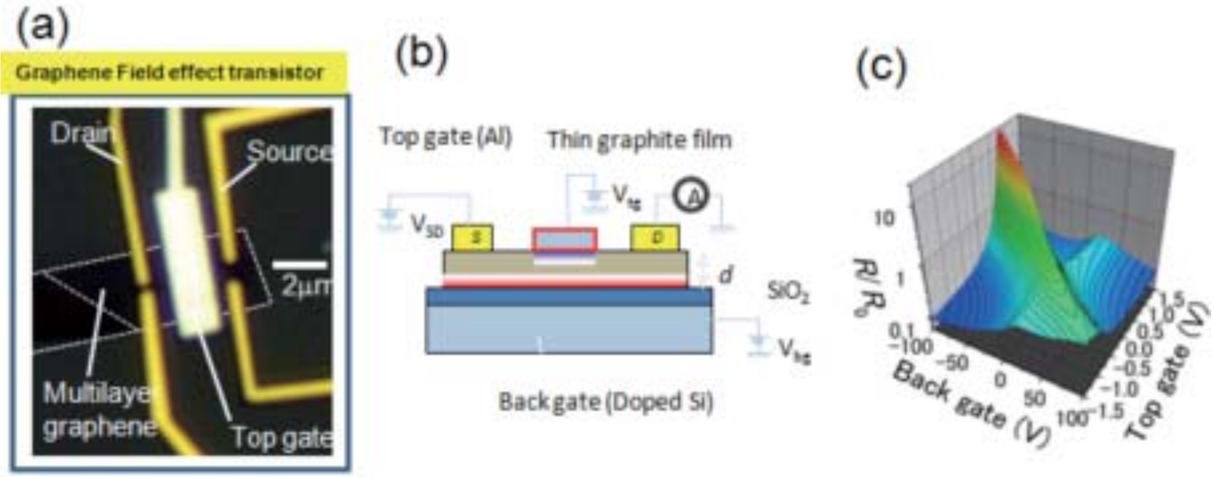

Fig. 1. Optical micrograph and schematic diagram of each fabrication step. An MLG flake was prepared on a SiO_2/Si substrate. Source and drain electrodes (Au/Ti) were deposited. An Al gate electrode was fabricated using the proposed method. An insulator layer was automatically formed at the interface between the graphene and the Al. The inner part of the Al electrode remained to be metallic. (b) Schematic of measurement configuration of the bilayer graphene gated by the Al top-gate and substrate back-gate. Electric conduction in the bi-layer graphene can be electrically tuned by the gates. (c) Resistance change depending on the top and back-gate voltages for bilayer graphene place on a 300 nm-SiO_2/Si substrate at 77 K. The resistance was normalized by the resistance R_0 at the point where the two peak ridges cross. Typical field effect mobility measured in a two-terminal monolayer channel was approximately 900 cm^2/Vs for holes and 500 cm^2/Vs for electrons. This is the first observation of the huge resistance enhancement with resistance change of over 400.

Bio-Inspired Materials for Sustainable Energy

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

1. Outline of Research

Our ultimate aim is to combine biological inspiration with electronics to give high efficiency materials and solar cells with applications to energy and sustainability. We will use a combination of self-assembly and directed assembly via lithography to create appropriate structures, taking our inspiration from biological systems. Our research combines experiment and theoretical modeling to give a detailed insight into the properties of the materials.

We have established a network of collaboration between three different institutions: MANA in NIMS, Nanoscience Centre in University of Cambridge and the London Centre for Nanotechnology in University College London. We are actively seeking to increase the collaborations between these sites and with other groups within MANA. In this year, we have arranged collaborative research visits to MANA for the co-director and the MANA Students as well as the first MANA-Nanoscience Workshop.

2. Research Activities

(1) Synthesis of metal oxide nanowires for DSSCs

We are developing novel methods to synthesize metal oxide nanowire structures for solar cell applications. Vertically oriented zinc oxide nanowires covered in a thin amorphous shell of zirconium oxide or magnesium oxide are grown using a hydrothermal method to be used as electrodes in DSSCs. Titanium dioxide nanowires can also be grown using a hydrothermal method. We will characterize and optimize the nanowire electrodes to allow flexibility in choosing an electrolyte with a suitable redox potential, hence achieving higher performance for dye solar cells. This is illustrated in Fig. 2.

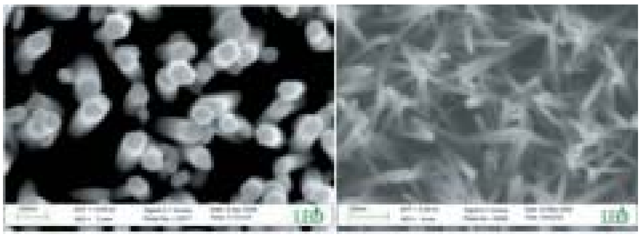

Fig. 1. Left – Hexagonal cross secion Zinc oxide nanowires grown using a hydrothermal method. Right - Square cross section Titanium dioxide nanowires grown using a hydrothermal method.

(2) Bonding of dye molecules to titania substrates

Using standard DFT, we are characterising the interaction of different dyes with TiO_2 surfaces found on nanoparticles [1]. We have investigated different binding sites on the surface, and shown that defect sites will bind the molecule strongly, but this may not be the ideal binding for efficient charge transfer. The highest occupied state and lowest empty state for coumarin bound to the rutile(100) surface are shown in Fig.2. We are also modelling the changes in electronic structure for indoline-based dyes with different functional groups in gas phase and on surfaces. In collaboration with NIMS we have also modelled a Ru-based dye bound to anatase and considered its dynamics. This exchange of expertise between different centres has been extremely beneficial.

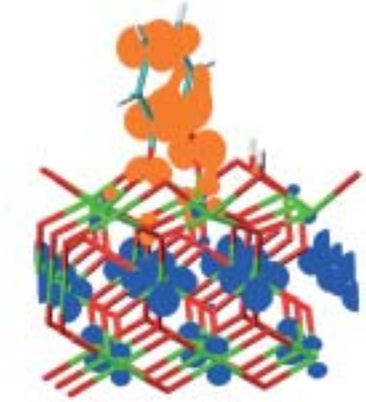

Fig. 2. LUMO (orange) and HOMO (blue) of coumarin adsorbed on TiO_2.

(3) Development of novel methods

Despite its success, DFT is not suitable for all applications, and we are developing novel approaches to extend the functionality of DFT for: large systems; energy levels; and charge transfer. It is hard to address large system sizes with standard implementations of DFT (which have a computer effort which increases with the cube of the number of atoms); we are using the Conquest linear scaling code (which has a computer effort that increases linearly with the number of atoms, and has been applied to systems containing millions of atoms) as a basis for this work. This code is the result of an on-going collaboration between NIMS and UCL. We have already implemented the constrained DFT technique for studying charge transfer excitations with the code, and are planning applications to indoline bound to anatase. We are also implementing time-dependent DFT within the code as a route to reliable energy level calculations for large systems.

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Construction of Interphases with Atomic/Molecular Order for Efficient Conversion of Energy/Materials

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MANA Scientist Hidenori Noguchi
MANA Research Associate Jian-Ding Qiu, Aleksandra Pacula

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 structure and electron transfer processes.

2. Research Activities

(1) Construction of catalytic interfaces by atomically ordered modification of metal surfaces with foreign metal[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 Pt50Ru50. 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. We have synthesized various metal complexes such as Pt-Pt, Pt-Ru, and Pt-Ni binuclear complexes. For example, Pt-Ru complexes 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.

We have also developed a novel method to form Pt (Fig. 1) and Pt-Pd nanoparticles with dendritic structure, which have very high surface area so that high catalytic activity is expected.

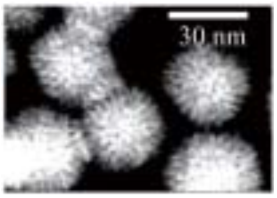

Fig. 1. TEM image of dendritic Pt nanoclusters.

(2) Photoenergy Conversion at Molecularly Ordered Modification of Semiconductor Surfaces

Hydrogen is the most important clean fuels in the future and production of hydrogen from water by solar energy is required. It is also important to form useful compounds by utilizing CO_2. Although photoelectrochemical (PEC) and photocatalytic decomposition of water and CO_2 reduction have been studied for long time, low conversion efficiency and low stability of the electrode are still serious problem. We have achieved the efficient PEC hydrogen evolution reaction (HER) and CO_2 reduction at p-Si(111) electrode modified with electron transport layer and metal nanoclusters (HER/CO_2 reduction catalyst). We have also constructed semiconductor/molecule interphase with photoswitching property.[2]

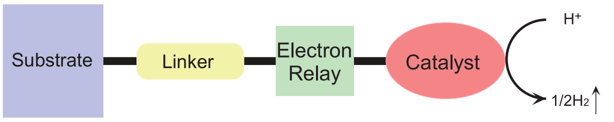

Fig. 2. Photoelectrochemical HER at p-Si(111) electrode modified with electron transport layer and metal nanoclusters.

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

To construct interfacial phases for highly efficient energy/materials conversion, it is essential to have information on the interfacial structure and electron transfer reaction. This year we studied humidity dependent water structure at Nafion, a polymer electrolyte membrane (PEM), surface by sum frequency generation (SFG) spectroscopy as shown in Fig.3 to understand the role of surface water in PEM fuel cell reaction.[3]

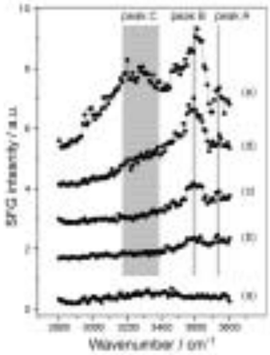

Fig. 3. Humidity dependent SFG spectra in OH region at Nafion surface.[3]

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Organic Solar Cells

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MANA Research Associate	Shang Gao, Keiichi Yoshimatsu Steffan Cook

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 like dye-sensitized solar cells (DSCs) and organic polymer solar cells. The main focus of our research here will be to

(1) understanding of key parameters determining the operation efficiency of the devices like electron transport properties and charge recombination process at the interfaces,

(2) development of new device structure and

(3) novel material synthesis based on the understanding of the device mechanism.

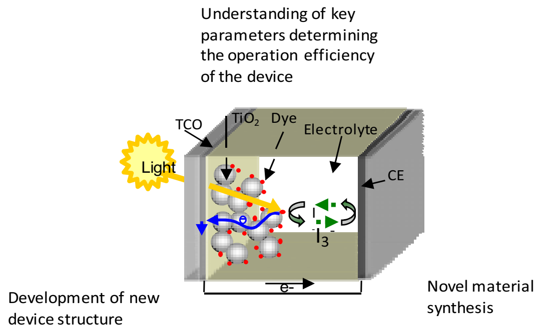

Fig. 1. Research and development feedback cycle.

2. Research Activities

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

In order to enhance power conversion efficiencies of DSCs, it is imperative to design novel sensitizers that exhibit an enhanced molar absorptivity in combination with a red-shifted absorption band. We have develop a new β-diketonato Ru(II) sensitizer 1 (Fig.2), which had a donor-conjugated antenna-triphenylamine (TPA) and exhibited a promising high absorption coefficient up to near IR region. We fabricated the DSC device with this new β-diketonato Ru(II) complex (Device 1), which exhibits a broad IPCE spectrum from 350 nm to 1000 nm and the IPCE values in 650 nm – 1000 nm region are apparently superior to those of device 2 with sensitizer 2. Notably, to the best of our knowledge, the IPCE onset (1000 nm) is the most red-shifted among all the DSC devices based on Ru(II) complexes.

(2) Estimate of singlet diffusion lengths in PCBM films by time-resolved emission studies

One important property of a material to be used in organic 'excitonic' solar cells, but that has not yet been measured for PCBM, is the materials exciton diffusion length. As excitons generated following light absorption must travel to an interface between donor and acceptor components in order to generate electrical charge carriers in the solar cell, materials with a long exciton diffusion length are desirable in order to achieve a high yield of electrical charge carrier production. Diffusion lengths for singlet states in PCBM films were estimated from analysis of annihilation rates in time-resolved emission studies. Our results show the onset of singlet annihilation in PCBM films at absorbed photon densities above 1 x 10^{18} per cm^3 and the singlet annihilation is well described by a time-independent value for the singlet annihilation rate constant of 0.5 x 10^{-9} cm^3 s^{-1}.(ref)

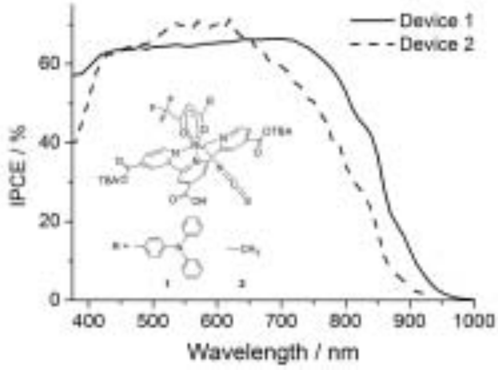

Fig. 2. The incident photon-to-current conversion efficiency (IPCE) spectra of devices 1 and 2.

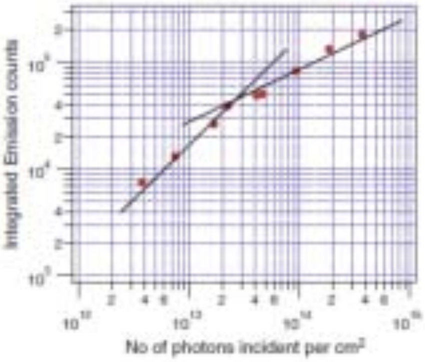

Fig. 3. Plot of the emission counts received from the PCBM film as a function of incident laser intensity. Black lines represent lines with a slope to the power of 1 and 0.5.

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Solid State Batteries

MANA Principal Investigator **Kazunori TAKADA**
MANA Scientist Tsuyoshi Ohnishi

1. Outline of Research

Lithium batteries have been powering portable electronics including cellular phones and note PC's. In addition, now they are expected to play new roles for the realization of a low-carbon society; electric vehicles will not be developed without high-performance batteries, and introduction renewable energy will not be promoted without energy storage device to stabilize interconnected power systems, for instance. However, the safety issue arising from their combustible organic electrolytes remains unsolved, which is an obstacle to increase the energy density and the battery size, because higher energy and larger size make the issue much more serious.

Solid electrolytes will make a breakthrough due to their non-flammability. In addition, single-ion conduction in solid electrolytes effectively suppresses the side reaction deteriorating battery performance. These features will pave the way to next-generation batteries. Our goal is to realize all-solid-state lithium batteries through the following researches on ionic conduction in solids.

2. Research Activities

(1) Research on interfacial ionic conduction

Ionic conductors often show anomalous ionic conduction at their surface or interfaces, which is categorized into "nanoionics". There are many interfaces in a battery, and nanoionics takes place in space-charge layers originated from different electrochemical potentials of the mobile ions at the hetero-interfaces. Since high electromotive forces of lithium batteries come from large difference of the electrochemical potential between the electrodes, nanoionics will be prominent in lithium systems.

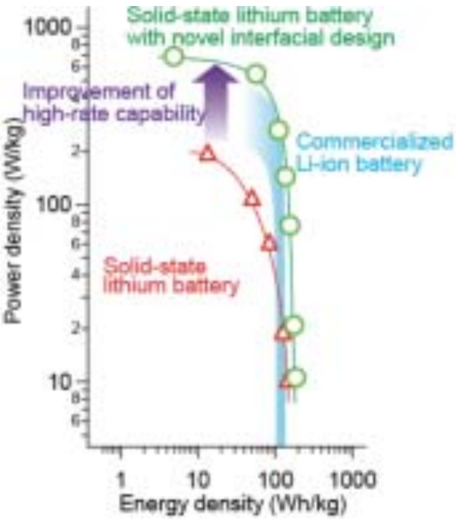

Fig. 1. Performance of solid-state lithium batteries was drastically enhanced by a novel interfacial design based on nanoionics.

In fact, a novel design of the interface structure based on the space-charge model drastically enhanced the power density of the solid-state lithium battery to be comparable to that of commercialized lithium-ion cells with liquid electrolytes as indicated in Fig. 1.1)

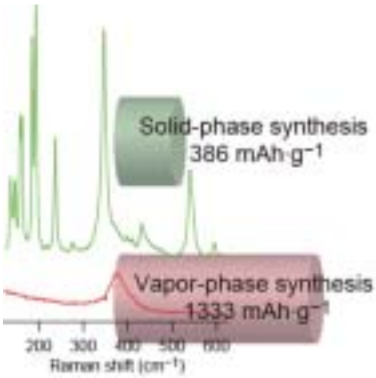

Fig. 2. The successive reaction from Li_2SiS_3 to Si – Li alloy was stabilized in a solid electrolyte. The electrode prepared by vapor-phase synthesis delivered much higher capacity than that by solid-phase synthesis.

(2) Novel electrode materials in solid-state systems

Although lithium-ion batteries have the highest energy densities among commercialized rechargeable batteries, much higher energy densities are required in the future uses. Some electrode reactions including alloying and conversion reactions are well known to deliver very high capacity but not practical. They are accompanied by pronounced morphological changes in the electrode, which make the reaction unstable and result in rapid capacity fading upon cycling.

One of the most distinguished features of solid electrolytes is that they are single-ion conductors; there are not mobile species other than lithium ions. Therefore, the above morphological changes will be suppressed in solid electrolytes to stabilize the reactions.

The example is Li_2SiS_3, which is expected to be successively converted into elemental silicon and alloyed into Si – Li upon the reduction to deliver a very high theoretical capacity of 1600 mAh·g^{-1}. A solid electrolyte stabilizes the successive reaction in a meta-stable structure electrode prepared by vapor-phase synthesis to realize high-capacity anodes (Fig. 2).2)

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

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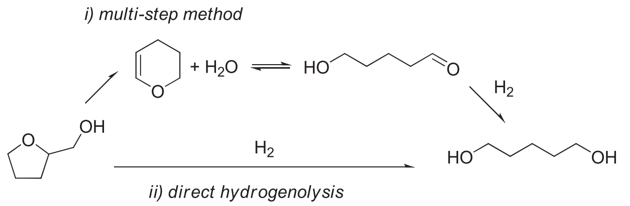
MANA Research Associate Yoshinao Nakagawa
Graduate Student Shuichi Koso

1. Outline of Research

The development of the transformations of non-food biomass to (petro)chemicals is an important sustainability issue. Since biomass-related raw materials usually have high oxygen content, useful oxygenates such as diols will be one of target chemicals derived from biomasses. α,ω-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 α,ω-diols from renewable resources has been needed, and one candidate among the α,ω-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. Two methods have been reported for the hydrogenolysis of tetrahydrofurfuryl alcohol: i) a multi-step method requiring the isolation and purification of intermediates and ii) direct hydrogenolysis. However, the selectivity to 1,5-pentanediol was low in the direct hydrogenolysis over conventional catalysts such as Cu-chromite. Therefore, it is necessary to develop more effective catalysts.



We have recently found that the Rh/SiO_2 catalyst modified with Re species is effective for the direct hydrogenolysis of tetrahydrofurfuryl alcohol[1]. However, this system has only limited catalyst stability. In 2009, we discovered that Rh/SiO_2 modified with Mo species is an active, selective and stable catalyst for the direct hydrogenolysis of tetrahydrofurfuryl alcohol to 1,5-pentanediol[2]. In addition, the catalysts for the glycerol hydrogenolysis[3], the preferential CO oxidation in H_2-rich stream[4], and the conversion of CO_2 to organic carbonates[5] were also developed.

2. Research Activities

(1) *Catalytic performance of $Rh\text{-}MoO_x/SiO_2$ in the hydrogenolysis of tetrahydrofurfuryl alcohol*[2]

The modification of Rh/SiO_2 with MoO_x (Mo/Rh=0.03-0.5) enhanced catalytic activity and selectivity to 1,5-pentanediol. The optimum amount of Mo addition was Mo/Rh=0.13 and the value was lower than that of Re addition (Re/Rh=0.5)[1]. The maximum 85% yield of 1,5-pentanediol on $Rh\text{-}MoO_x/SiO_2$ (Mo/Rh=0.13) was attained at 24 h reaction time. In contrast, the maximum yield of 86% on $Rh\text{-}ReO_x/SiO_2$ was attained at 36 h. While the activity of $Rh\text{-}MoO_x/SiO_2$ was slightly lower than that of $Rh\text{-}ReO_x/SiO_2$ when the conversion level was not high, $Rh\text{-}MoO_x/SiO_2$ showed much higher activity than $Rh\text{-}ReO_x/SiO_2$ in very low concentration of tetrahydrofurfuryl alcohol, which can explain the shorter reaction time for the highest yield on $Rh\text{-}MoO_x/SiO_2$. The catalysts were reused repeatedly in order to evaluate the stability. The activity and selectivity of the $Rh\text{-}MoO_x/SiO_2$ catalyst were not changed in five runs (53±1% conversion and 94±1% selectivity to 1,5-pentanediol).

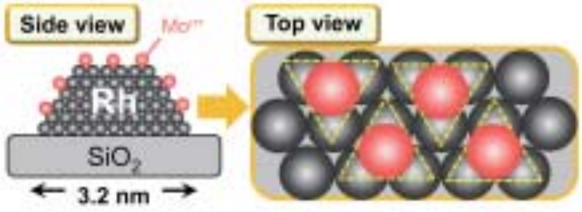


Fig. 1. Schematic view of $Rh\text{-}MoO_x/SiO_2$ catalyst.

(2) *Structure of $Rh\text{-}MoO_x/SiO_2$*[2]

The average particle size of $Rh\text{-}MoO_x/SiO_2$ was almost the same (ca. 3 nm) as those of Rh/SiO_2 and $Rh\text{-}ReO_x/SiO_2$ by TEM observation and XRD. The CO adsorption on $Rh\text{-}MoO_x/SiO_2$ was significantly lower than that of Rh/SiO_2 and almost the same as that on $Rh\text{-}ReO_x/SiO_2$ with the same molar ratio of additive/Rh. The curve-fitting results of Mo *K*-edge EXAFS of $Rh\text{-}MoO_x/SiO_2$ (Mo/Rh=0.13) showed the presence of the Mo-O (CN=1.1) and Mo-M bonds (M=Mo or Rh; CN=3.0). The CN of the Mo-M bond is comparable to that of the Re-Rh bond (3.6) found in the EXAFS analysis of $Rh\text{-}ReO_x/SiO_2$ where ReO_x clusters are formed on the surface of Rh metal particles. These data suggest that monomeric MoO_x species were absorbed on the surface of Rh metal particles. The interaction between Rh and MoO_x can be related to the cooperative function as follows: tetrahydrofurfuryl alcohol is adsorbed on MoO_x species via the OH group and the hydrogenolysis of the C-O bond catalyzed by neighboring Rh surface. The isolated Mo species can give larger interface between Rh metal and MoO_x species than the ReO_x cluster, which may explain the smaller optimum amount of Mo additive than Re additive.

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Nanostructured Materials for Solid Oxide Fuel Cells and Sustainable Development

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MANA Research Associate Lei Bi, Edoardo Magnone, Corrado Mandoli, Ziqi Sun

1. Outline of Research

World population raise and the need for improving the quality of life of a still large percentage of human beings are the driving forces for searching alternative, sustainable energy production systems. Fuel cells are promising, given their low environmental impact and high chemical-to-electrical energy conversion efficiency. Solid oxide fuel cells (SOFCs) are the most promising fuel cells for stationary energy production, although recently miniaturized SOFCs for portable power generation have raised interest, since they are likely to produce energy densities per volume and specific energy per weight up to four times larger than the state-of-the-art batteries 1).

Aim of the MANA research project is the fabrication of micro-SOFC devices (Fig. 1), via the understanding of nanostructured materials performance as single component or in assemblies. Pulsed laser deposition (PLD) is used for the fabrication of tailored oxide thin films for SOFCs, because it allows obtaining single crystal or polycrystalline films 2), with tailored microstructure from dense to highly porous. High temperature protonic conductors (HTPCs) are used as electrolytes, with focus on chemically stable materials, such as Y-doped barium zirconate (BZY). Suitable electrode materials are studied to improve the performance of fuel cells based on HTPCs, based on the development of mixed protonic-electronic conductors 3).

In a global view of exploiting nanomaterials for a sustainable development, interdisciplinary research is also pursued in the biomedical field. Population aging affects sustainable development, since healthcare treatments are needed to improve elder people quality of life. For this aim, scaffolds for cardiac tissue engineering are studied for regenerative medicine.

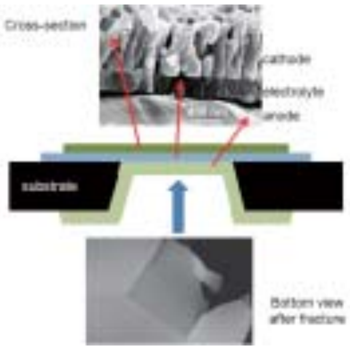

Fig. 1. Schematic diagram of the design of microfabricated μ-SOFCs based on a free-standing electrolyte membrane with anode and cathode layers 1).

2. Research Activities

Our research activities can be summarized as follows:

(i) Study of thin film electrolyte for micro-SOFCs, deposited by PLD 4).
(ii) Development of new, chemically stable materials for HTPC electrolytes.
(iii) Development of new cathode materials with low area specific resistance at low temperatures 5).
(iv) Design of highly porous 3D scaffolds for soft tissue engineering 6).

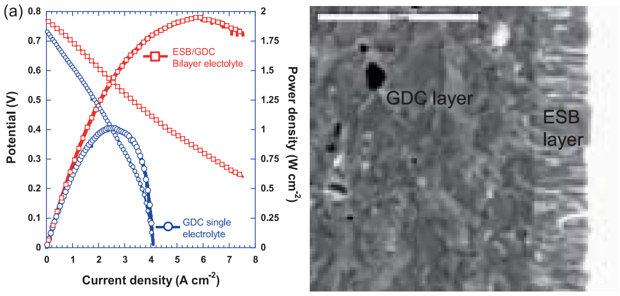

Fig. 2. Electrochemical performance (left) and SEM cross- section (right) of CGO/ESB bilayer 4).

(1) High Performance Bilayered Electrolyte Intermediate Temperature Solid Oxide Fuel Cells 4)

We showed that coupling in a bilayer structure Gd-doped ceria (CGO) at the cathode with erbia-stabilized bismuth oxide (ESB) film prepared by PLD at the anode side led to a very efficient electrolyte design that allowed to reach 2 W/cm^2 at 650°C, doubling the power density output obtained for a SOFC with a single CGO layer.

Fig. 3. Healthy thick tissue (left) after 14 DIV on 3D PLLA scaffold fabricated by thermally induced phase separation (right).

(2) Thick Soft Tissue Reconstruction on Highly Perfusive Biodegradable Scaffolds 6)

We prepared by directional thermally induced phase separation 1 mm-thick 3D scaffolds made of PLLA with an overall porosity of 93% and an interconnectivity of 90%. After seeding with stem cells, healthy, confluent tissues were reconstructed after 14 days in vitro static culture, exploiting the highly porous microstructure of the engineered scaffolds.

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Reticular Materials

MANA Principal Investigator **Omar M. YAGHI**
MANA Scientist Kentaro Tashiro
MANA Research Associate Pothiappan Vairaprakash, Hisanori Ueki

1. Outline of Research

The synthesis of mononuclear metal complexes by design is a well-established process. In sharp contrast, however, a protocol for the synthesis of complexes containing multiple homo- or hetero-metals, in a designed fashion, remains largely absent so far, where it is inevitable to get a mixture of products with respect to the number, nuclearity, or sequence of metal centers (Figure 1; upper part). In this project, we will intend to develop a conceptually new synthetic methodology to create metal complex arrays with controlled number, nuclearity, or sequence of metal centers (Figure 1; lower part). This methodology will open a new era of metal complex-based materials science by producing multimetallic systems that are inaccessible via traditional synthetic methodologies. Especially, the controlled sequence of metal centers in the arrays, like those in proteins and nucleic acids, will be the most attractive characteristics of this type of materials. Moreover, since our methodology is potentially extendable to automated, parallel processes, high-throughput preparation of the libraries of metal complex arrays will be expected. By taking advantage of such features, we will, in the next step, challenge to create catalysts having extraordinary high and unique activity, selectivity, and tunability, which should make a great contribution to realize our future sustainable life.

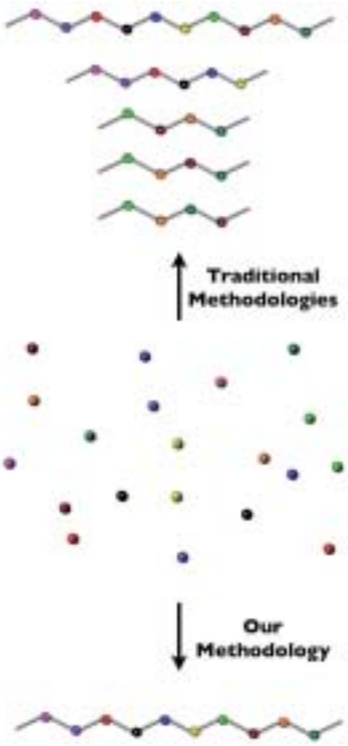

Fig. 1. Schematic representation of the possible multimetallic products *via* traditional and our methodologies.

2. Research Activities

(1) Design of Monomeric Metal Complexes for the Synthesis of Multimetallic Complex Arrays[1)]

We have prepared a series mononuclear metal complexes with a newly designed organic moiety, and after thorough screening, we found that complexes with Pt(II), Rh(III), Ru(II), and Ir(III) (Figure 2) are suitable for our project. These metal complexes can be obtained in gram quantity and exhibit small ligand exchange activity that allows their stepwise linkage to form metal complex arrays with a controlled sequence.

Fig. 2. Monomeric metal complexes suitable for this project.

(2) Synthesis of a Series of Multimetallic Complex Arrays[1)]

By using the monomeric metal complexes as shown in Figure 2, we attempted to synthesize a series of multimetallic complex arrays to check the availability of our new methodology. After optimizing the synthetic conditions, so far, we have successfully prepared dimeric, trimeric, tetrameric, pentameric, and hexameric homometallic arrays of the Pt complex (Figure 3; left side). Our methodology is also applicable to the synthesis of heterometallic arrays, as demonstrated by the production of several dyads and triads containing two or three different kinds of metal ions (Figure 3; right side).

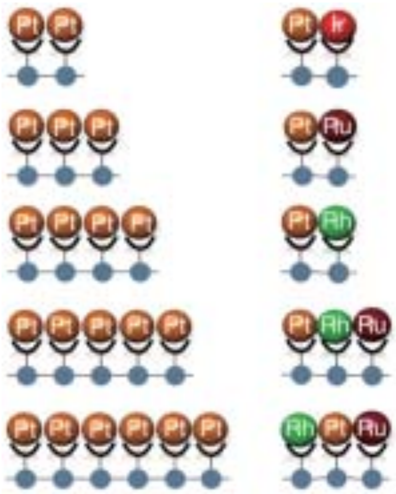

Fig. 3. Multimetallic complex arrays synthesized by our methodology developed in this project.

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Nanoarchitectonics of Hybrid Artificial Photosynthetic System

MANA Principal Investigator **Jinhua YE**
MANA Research Associate Y. Bi, H. Tong, M. Amina,
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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.

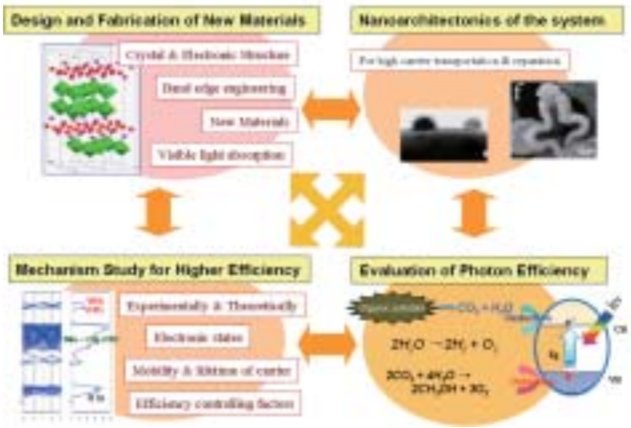

Fig. 1. Four sub-themes and their organic coordination for conducting effective materials exploration research.

2. Research Activities

(1) Novel visible light active photocatalysts for efficient environment remediation$^{1\text{-}3)}$*:*

A novel photocatalyst Ag_2GeO_3 was developed1), where the active wavelength extends up to 660 nm, covering the main components of the solar spectrum and indoor illuminations. The photocatalyst exhibited excellent activities in photodegradation and mineralizations of various organic dyes, even under weak light irradiation of white fluorescent lamp (Fig.2). The high performance can be reasonably attributed to its unique crystal and electronic structures, and demonstrate a great potential of the material to be applied for waste water treatment.

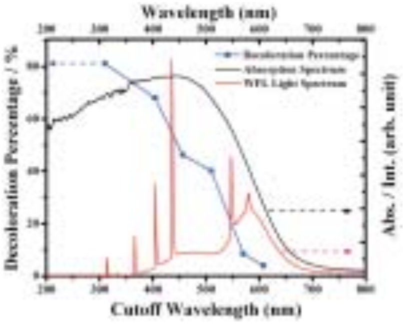

Fig. 2. The activity in MB photodegradation over the new material, shown together with the spectrum of WFL light.

(2) Advanced photocatalytic property explored by Nanoarchitectonics$^{4)}$*:*

We have developed a facile and effective approach for preparing core–shell Ag/AgCl hetero-nanowires with uniform structures by an in-situ oxidation reaction between pentagonal Ag nanowires and $FeCl_3$ solution at room temperature (Fig. 3). The morphologies and structures of the obtained nanoproducts were found to greatly depend on the redox potential of both Ag species and metal ions. These novel hetero-nanowires exhibit excellent photocatalytic performance for decomposition of methylic orange under visible-light irradiation, and the activity has a strong correlation with the core-shell constitutions.

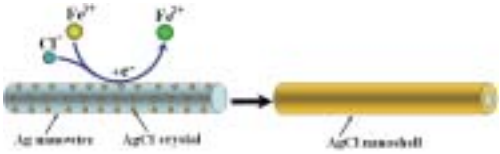

Fig. 3. Schematic illustration of the in-situ oxidation process for Ag/AgCl core-shell nanowires.

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Electrochemical Nanobio-Sensing Devices

MANA Principal Investigator **Yuji MIYAHARA**
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1. Outline of Research

Electrostatic interaction between biomolecules and electrons in semiconductor materials is investigated combining field-effect semiconductor devices and biotechnology. By controlling interfaces among biomaterials, organic molecules and semiconductor devices, biomolecular recognition and cell function are detected without labeling materials and non-invasively. Since bio-sensing devices using nano/micro fabrication technologies are easily miniaturized and integrated, they are useful for high throughput screening in regenerative medicine and drug development. Interdisciplinary field between biotechnology and electronics will be explored and developed through investigation on principles of bio-transistors.

The electric charge of lipids plays crucial roles in biochemical processes. Anionic lipids are ubiquitous in nature and regulate various cellular functions such as DNA replication and protein translocation. Cationic lipids are found in certain membranes and have been used in various transfection and gene therapy applications. Such charged lipids can sometimes be incorporated into supported lipid bilayers (SLBs) by vesicle fusion. Since SLBs are useful in vitro mimics of biological membranes, their properties and formation mechanisms have been widely studied by monitoring various signals including fluorescence, mass, viscoelasticity, refractive index, topography, and impedance. We detect SLBs through their charge using field-effect devices.

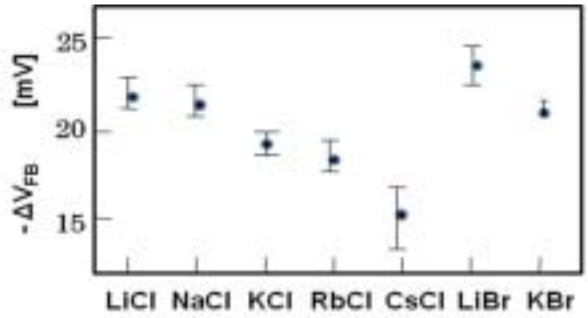

Fig. 1. Flat-band voltage change upon SLB formation.

2. Research Activities

The adsorption of supported lipid bilayers (SLBs) with positive charge onto field-effect devices was studied using various salt solutions to understand the signal generation mechanisms of the devices. The flat-band voltage change ($-\Delta V_{FB}$) which occurred upon SLB formation was dependent on the type of monovalent cations contained in solution. As shown in Fig. 1, we have demonstrated that the flat-band voltage change which occurs upon SLB adsorption decreases in the sequence of $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$. Zeta potential data showed that the intrinsic charge of bilayers was almost constant in the presence of any alkali ions examined. The results suggest that the charge of lipids does not solely determine the flat-band voltage. The binding affinity of alkali ions to silicon nitride showed a similar trend to the dependence of the flat-band voltage change on alkali ions. The results indicate that the specific interaction of small inorganic ions with the device surface significantly influences the magnitude of signal response upon SLB formation[1]. It seems that salt ions specifically bound to the device surface and the charge of bilayers both contribute to the signal generation mechanisms.

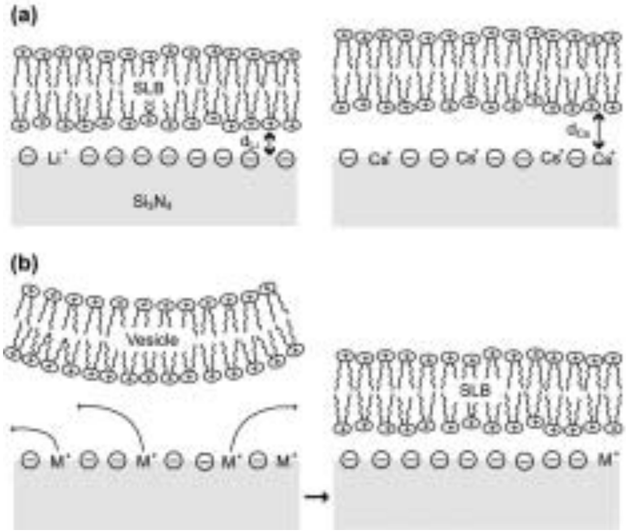

Fig. 2. Possible mechanisms to explain the dependence of the $-\Delta V_{FB}$ on monovalent cations.

The cation-dependent flat-band voltage shift is expected to occur due to the specific binding of alkali ions to silicon nitride. The difference in the bilayer-sensor separation and the desorption of alkali ions from the sensor surface were proposed as possible mechanisms to explain the flat-band voltage shift varying with the cationic species, as illustrated in Fig. 2. We have also shown that the Br^- ions specifically bound to the vesicles are removed from at least the lower leaflet during SLB formation.

The removal of the cations and anions from silicon nitride and the vesicle surface seems to occur to enhance the electrostatic interaction between the cationic bilayers and the anionic silicon nitride surface.

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Design of Stable-Radical-Containing Nanoparticles (RNP)

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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) as well as magnetic resonance (MR), it is anticipated as an EPR and MR imaging probes. 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 and/or potassium 4-TEMPO alkolate to obtain amphiphilic block copolymer possessing stable free radicals in the hydrophobic segment (PEG-*b*-poly(PCTEMPO_N) and PEG-b-TCTEMPO_O). These block copolymers in aqueous media forms stable polymeric micelle, which contains ca. 2,000 stable radicals in the core (stable-radical-containing-nanoparticle N and O (RNP_N and RNP_O)). In this year, we focused on preparation and characterization of RNP-O in order to improve bioavailability as well as imaging characteristics.

We set following themes of the RNP_O 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* MR imaging probe

2. Research Activities

The size and polysispersity factor (μ_2/Γ^2) of RNP_O was estimated by dynamic light scattering (DLS) measurements to be ca. 40 nm and 0.106, respectively. The EPR signal of O-RNP showed broad signal in aqueous media, indicating the confinement of nitroxyl radicals in the core of block copolymer micelle.

The reduction resistivity of TEMPO radicals in the O-RNP core was compared with TEMPOL. Figure 2a shows time-course of the EPR signal intensities of O-RNP and TEMPOL. When the free-TEMPOL solution was monitored in the presence of 3.5 mM AsA, the signal intensity rapidly decreased. On the contrary, the EPR signal intensity of O-RNP decreased very slowly, indicating that the TEMPO radicals in O-RNP resisted reduction even in the presence of 3.5 mM AsA. In addition, the blood circulation of TEMPO radicals in the O-RNP core was evaluated. The EPR signal in bloodstream of mice was observed even 24 h after tail vein injection. It is sharp contrast against TEMPOL, which almost disappeared within 2 min in bloodstream (Fig. 2b). The half-life of the O-RNP was 240 times longer (60 min) than that of TEMPOL.

In addition, T1-weighted MR imaging of tumor-bearing mouse after the administration of RNP_O is measured. As shown in Figure 3, RNP_O selectively provided high contrast at solid tumor site (tumor leg 1). In contrast, signal intensity of normal tissue area drastically decreased. This result suggests that RNP_O reduced the nonspecific accumulation in normal tissues and increased preferential accumulation in tumor tissues due to the enhanced permeability and retention effect. On the other hand, the signal intensity of another tumor area (tumor leg 2) also drastically decreased similar to normal leg. Although this reason is still under investigation, this area might be a strong reducing environment.

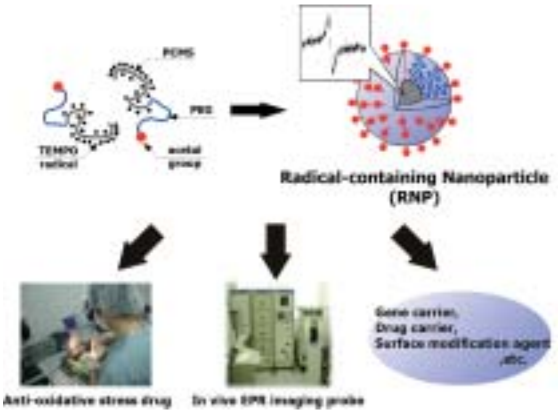

Fig. 1. The themes of the RNP and their organic coordination.

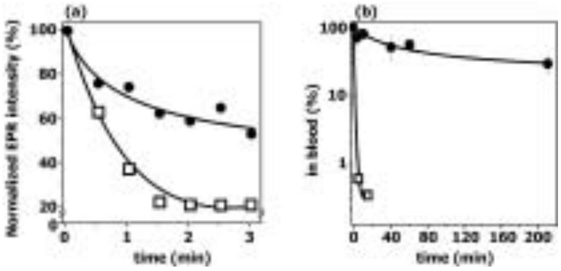

Fig. 2. (a)Time-course of EPR signal intensities of O-RNP (●) and TEMPOL (□) in the presence of 3.5 mM AsA (Temperature, 23 °C) (b) The blood circulation of TEMPO radical in the O-RNP core (●) and TEMPOL (□).

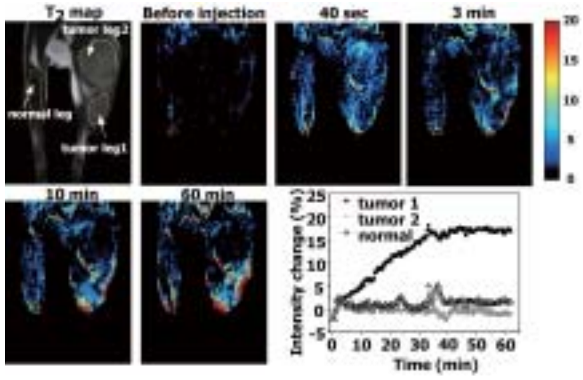

Fig. 3. T1-weighted image of tumor-bearing mouse after the administration of O-RNP.

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, but those 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.

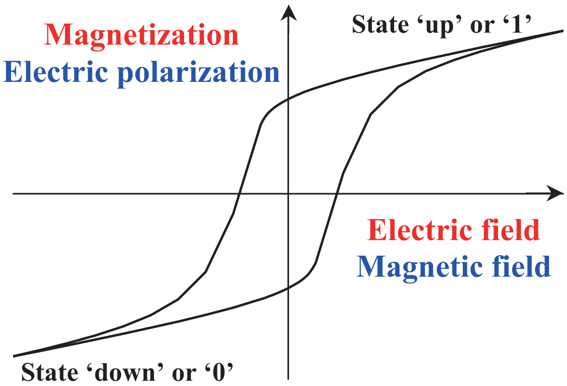

Fig. 1. Ferroelectric/ferromagnetic hysteresis loop: the basis of many memory elements.

2. Research Activities

(1) Development of new near-room-temperature multiferroics.[1)]

Using high pressure, we could prepared new perovskite materials $(In_{1-x}M_x)MO_3$ (M = Mn and $Mn_{0.5}Fe_{0.5}$) (Fig. 2). They turned to be multiferroics possessing spontaneous polarization and magnetism near room temperature (RT). Our results give a significant contribution to the development of RT multiferroics and open wide possibilities for thin-film research and future improvement of In-based perovskites. Our results also show new ways for the preparation of perovskite-type materials.

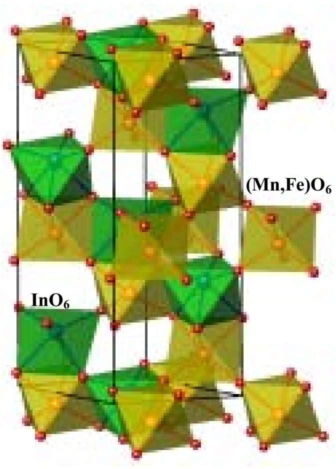

Fig. 2. Crystal structure of $(In_{1-x}M_x)MO_3$ M = $Fe_{0.5}Mn_{0.5}$, $x = 0.176$.

(2) Investigation of high-pressure behavior of ferroelectric and multiferroic materials $BiMO_3$.[2)]

We found new modifications of $BiMO_3$ at high pressure. These results are helpful for understanding the origin of ferroelectric distortions and finding ways to stabilize new high-pressure phases at ambient conditions.

(3) Discovery of new unusual magnetic material $Bi_3Mn_3O_{11}$.[3)]

We prepared a new phase at high pressure $Bi_3Mn_3O_{11}$. This phase shows interesting magnetic properties. In addition, the oxygen content of this compound can vary in a wide range significantly modifying its magnetic properties but keeping the same framework structure.

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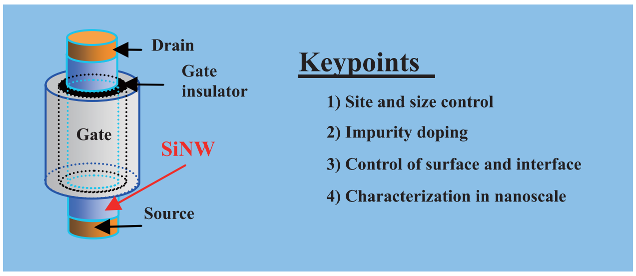
Next-Generation Semiconductor Nanomaterials and Nanodevices

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 semiconductor nanowires (Fig. 1) have been suggested as the basis for next-generation semiconductor devices.

In order to realize the next-generation vertical-type MOSFETs, 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 and P) 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.



Keypoints

1) Site and size control
2) Impurity doping
3) Control of surface and interface
4) Characterization in nanoscale

Fig. 1. Illustration of vertical-type MOSFETs.

2. Research Activities

(1) Synthesis of GeNWs

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 grow defect-free GeNWs with uniform diameter, I applied the UHV-CVD method this time (Fig. 2).

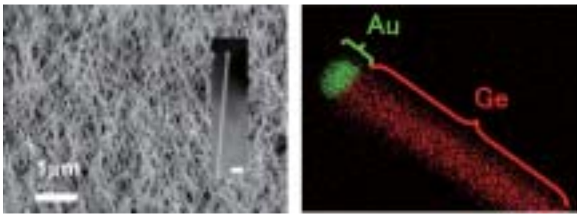


Fig. 2. SEM and TEM images of GeNWs. The EDX result is also shown.

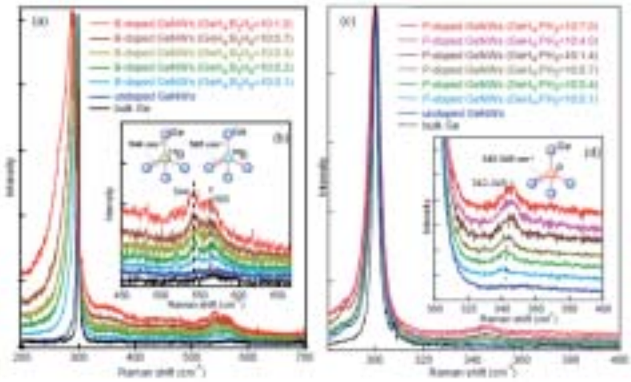


Fig. 3. (a) Raman spectra observed for B-doped GeNWs. (b) The magnification of (a). (c) Raman spectra observed for P-doped GeNWs. (c) The magnification of (d).

(2) Doping of GeNWs

I have already succeeded in proving the formation of p-type and n-type SiNWs by Raman scattering measurements.1-4) I also applied the same technique to the characterization of impurity doping in GeNWs. Micro-Raman scattering measurements were performed for B-doped GeNWs (Figs. 3 (a) and (b)). The intense peak at about 300.2 cm^{-1} is attributed to the Ge optical phonon peak. This peak comes from the crystalline Ge core of GeNWs. Two peaks were observed at about 544 and 565 cm^{-1}. The peak intensity increased with increasing B_2H_6 gas flux. The intensity ratio is estimated as being roughly 4:1, which is in good agreement with the natural abundance of the two isotopes of ^{11}B (80.2 %) and ^{10}B (19.8%). These results proved the peaks are due to the B local vibrational peaks. The optical phonon peak also showed a broadening toward lower wavenumber, which is attributable to the Fano effect, showing that B atoms are electrically acivated in GeNWs. These result clearly show that B atoms were doped and electrically activated in the substitutional sites of crystalline Ge core region of GeNWs, namely the formation of p-type GeNWs.

Figures 3 (c) and (d) show the result of P doping in GeNWs. As well as the B-doped GeNWs, I could observe P local vibrational peak and the Fano broadening in the Ge optical phonon peak. These result prove that P atoms were clearly doped in substitutional sites of the crystalline Ge core of GeNWs, resulting in the formation of n-type GeNWs.

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Device Application of Organic-Metallic Hybrid Polymers for Electronic Paper

MANA Independent Scientist Masayoshi HIGUCHI

1. Outline of Research

Electronic paper (e-paper) is a flexible display capable of holding images even after the power is turned off. It is thus an energy- and resource-saving device with a potential to replace newspaper and other paper media. Researchers, however, have been struggling to make color, as opposed to black-and-white, e-paper. Among different types of e-paper, electrochromic e-paper seems most promising as color displays but its development has been hampered by poor durability and difficulty of use in solid-state devices. We synthesized a novel electrochromic polymer and used it to produce a multi-color display.

2. Research Activities

(1) Organic-metallic hybrid polymers are obtained quantitatively by complexation of metal ions such as iron, cobalt, or ruthenium, and organic ligands bearing several coordination sites such as bis-terpyridines (Figure 1). The hybrid polymers have a specific color based on the metal-to-ligand charge transfer (MLCT) absorption from the metal ions to the terpyridine parts of the organic ligand in the hybrid polymers. Interestingly, a polymer film cast on an ITO electrode exhibits excellent electrochromic properties: the color of the film disappears when a higher potential than the redox potential of the metal ions is applied to the polymer film. On the other hand, the film returns to its original color when a reductive potential below the redox potential of the metal ions is applied. Various colors such as purple, blue, red, and orange can be expressed by changing the metal species and/or by modifying the organic modules.

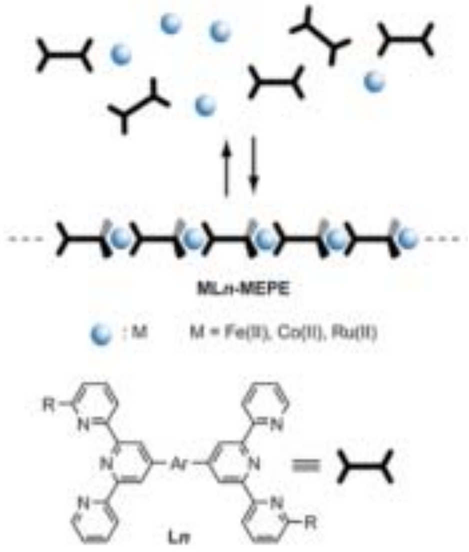

Figure 1. Organic-metallic hybrid polymers.

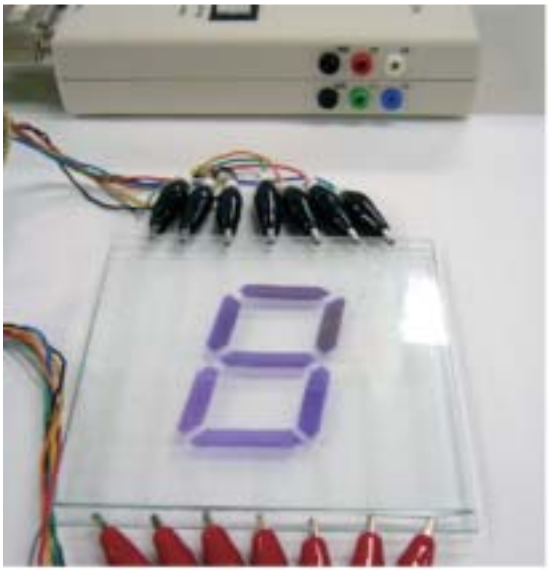

Figure 2. An electrochromic device using the hybrid polymer.

(2) A solid-state electrochromic device was developed using a mixture of polymethylmethacrylate, propylene carbonate, and LiClO4 as the polymer gel electrolyte. The details of fabrication are as follows: 20 µL of a methanol solution (1.0 mg the polymer/0.5 mL MeOH) is cast or spin-coated (500 rpm for 60 s) on ITO electrodes (20Ω). A mixture of polymethylmethacrylate (7.0 g), propylene carbonate (20 mL), and LiClO4 (3.0 g) was used as the polymer gel electrolyte. The film changes from colorless to blue faster (within one second) than vice versa (a few seconds), probably because Fe(II) is more stable than Fe(III) in the polymer. We fabricated electrochromic 10-inch solid-state devices equipped with two polymer films, which can exhibit two different displays by reversing the direction of current. Therefore, the device equipped two Ru/FeL1-MEPE films (Ru/FeL1-MEPE is a copolymer of RuL1-MEPE and FeL1-MEPE bearing 1,4-bis(2,2′:6′,2″-terpyridin-4-yl)benzene as the organic ligand) has five kinds of displays that can be activated changing the applied potentials between –3 and 3 V; this is because Ru/FeL1-MEPE films exhibit different colors such as red, orange, and pale green at 0, 1.8, and 2.5 V, respectively. Recently, we also succeeded in fabricating degital display using the hybrid polymers (Figure 2).

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Quantum-Dot Devices in Graphene

MANA Independent Scientist Satoshi MORIYAMA

1. Outline of Research

Graphene, a single atomic layer of graphite, and few-layer graphene (FLG) sheets are one of the attractive two-dimensional (2-D) conducting materials for a new stage of low dimensional physics. Electronic properties are expected to differ from the well studied case of the 2-D electron gas in semiconductor hetero-structure. These differences are due to the unique band structure of graphene, so-called 'Dirac Cone', which exhibits electron-hole degeneracy and vanishing carrier mass near the point of charge neutrality. From the application point of view, the ballistic transport and high mobility in graphene and FLG make them possible candidates for future electronic quantum 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) Coupled quantum dots in a graphene-based two-dimensional semimetal [1)]

We have shown the demonstration of double quantum-dot devices in triple-layer graphene, 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 the quantum computation and the quantum cellular automata. Graphene and FLG samples are prepared by micromechanical cleavage of graphite crystals and deposited on the surface of a silicon substrate with a 290 nm thickness of oxidized silicon. Optical microscope contrast and Raman spectroscopy measurements can be identified the single-, double-, triple-, and few-layer graphene flakes on the substrate. From the micro-Raman spectroscopy, we confirmed that our working devices were fabricated on a triple-layer graphene (TLG) sheet. By using electron-beam lithography techniques, a double-dot device structure was patterned into a thin resist that protected chosen areas during oxygen reactive ion etching process. Figure 1 shows the scanning electron microscope image of the fabricated double-quantum- dot device. The device consisted of triangular-shaped two islands as quantum dots (the area $S \approx 0.005\ \mu m^2$), connected via two short constrictions to wide source and drain regions. The connected constrictions were about 20 nm in length and 15 nm in width. These constrictions were expected to act as tunnel barriers due to the quantum size effect. Three lateral graphene side gates have been fabricated close to the active graphene structure.

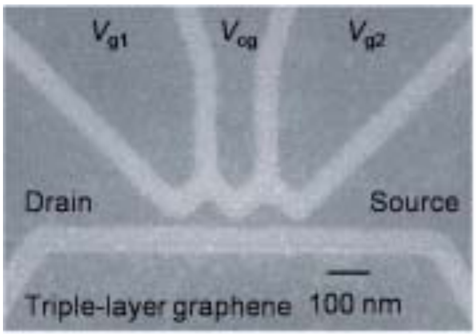

Figure 1. Scanning electron microscope image of the measured device with electrode assignment. Bright areas show etched triple-layer graphene.

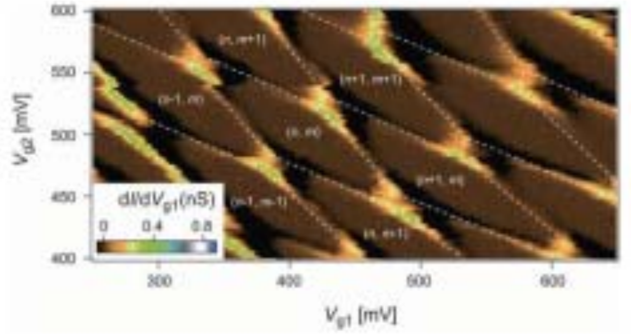

Figure 2. Experimental charge stability diagrams for series-coupled quantum dots with weakly tunnel-coupling regime.

Low temperature transport results reveal that the device acts as single-electron transistors in which the electrons though the quantum dots flow one by one. Figure 2 shows an experimental charge stability diagram. Honeycomb structures in this mapping, which are characteristic of coupled quantum dots, are clearly observed. The experimental results revealed the honeycomb charge stability diagrams from weak to strong interdot tunnel coupling regimes.

The research has shown the possibility of developing integrated nanodevices using graphene, it is expected to contribute to progress in single electron electronics, and the development of novel functional nanoelectronics, so-called "Beyond CMOS" including quantum information processing.

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Electronic Excitations in Nanoscale Objects: Infrared Plasmons and Applications

MANA Independent Scientist **Tadaaki NAGAO**
MANA Research Associate Dominik Enders, Gui Han, Osamu Saito

1. Outline of Research

The technology for amplifying, confining, and scattering the light in nanoscale objects is strongly desired as a key technology for future optical communication and sensing. By hybridizing the plasma oscillation with the electromagnetic field near the metal surface we can manipulate the light at a much shorter wavelength than that in free space. Such hybridized waves with contracted wavelength are called plasmon polaritons.

When the size of the object shrinks beyond the micrometer scale and when it reaches down to the nanometer or sub-nanometer scale, novel effects that originate from its smallness and its shape come into play. Atom-scale size effects become especially pronounced in metallic objects, since the Fermi wavelengths of typical metals are in the Ångström range. Plasmon polaritons in metal nanostructures show maximum tunability by changing the shape, the size, and thus the dimensionality of the objects. Such feature can be utilized for tailoring optical properties for future nano-photonics/optics devices for information technology as well as high-sensitivity sensors and efficient catalytic materials.

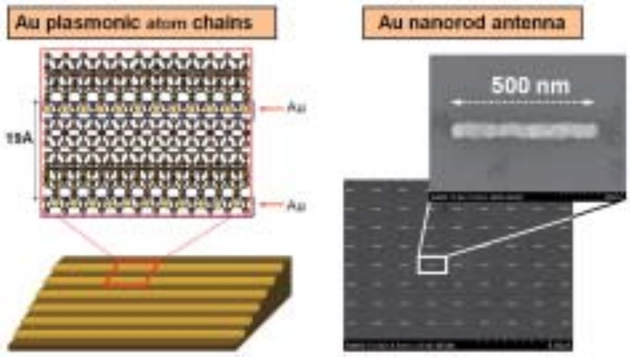

Fig. 1. (Left) Atomic-scale structure of a self-assembled one-dimensional atom chain (schematic diagram)
(Right) Nanoscale one-dimensional nanoantenna of gold prepared by electron lithography (SEM photo)

2. Research Activities

By utilizing bottom-up nanofabrication techniques such as ultrahigh-vacuum MBE growth on template crystal surfaces, we have produced 1D, 2D, and 3D patterned "atomic-scale low- dimensional" metallic nanostructures with precise controlling of its crystallinity and sizes. By "molding" the plasmons into size/shape controlled small objects, we aim to explore and freely design the dielectric and optical properties of nanostructures for future photonic applications. For the genuine low-dimensional systems such as atom chains, and atom sheets, nearly no fundamental knowledge on plasmon has been available and we experimentally explored these systems in detail.

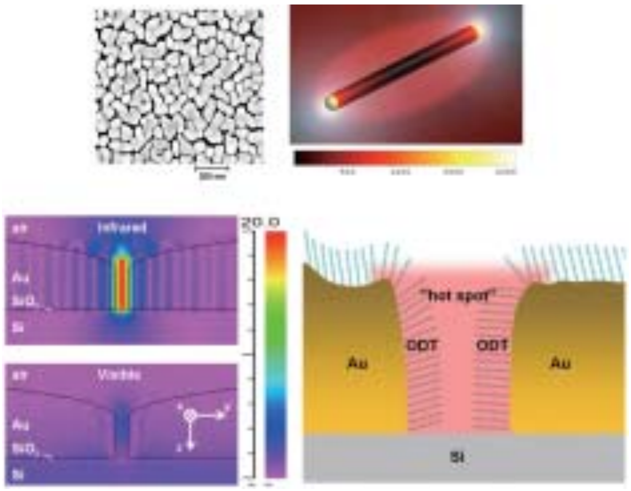

Fig. 2. (Top) Examples of structure-optimized SEIRA active Au nanostructures. (Lower left) Electric field calculations of a nanogap between the Au nanoisland ensamble
(Lower right) Schematics of the thiol molecules adsorbed at the island surfaces.

Also, shape-controlled quasi-2D metal-nanoisland array (such as grown by MBE or by the wet-chemistry route) are of special technological importance but not yet studied systematically in a quantitative manner. Their plasmon resonances are related to strong nearfield enhancement, which enables surface enhanced IR absorption (SEIRA), and we aim at developing these SEIRA-active device structures for chemo/biosensing applications. Since plasmonic interaction of well-defined specially shaped 3D gold nanostructures with vibration modes may give even higher SEIRA, we also study top-down lithographic structures in order to reach a maximum SEIRA effect.

In our project, we target

1) Mesoscale plasmonic structures for infrared chemo/biosensors with attomol sensitivity and quantitative analysis.
2) Nanoscale plasmonic structures for antenna resonances in mid-infrared spectral range.
3) Atom-scale metallic structures for exploiting plasmonic excitation, and propagation, confinement, and cavity effects in ultimately tiny systems.

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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. The major purpose of the present study is to develop chemically functionalized biointerfaces with photochemically active compounds and apply them for controlling cellular functions[1] as well as for engineering tissue mimics *in vitro* (Fig. 1). This year, we also developed a new method for the chemical modification of plastic surfaces by an atmospheric plasma treatment.

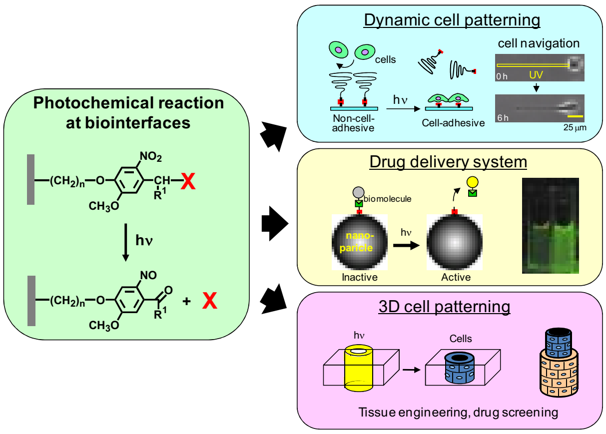

Fig. 1. Photoresponsive biointerfaces developing in this study.

2. Research Activities

(1) *Silane coupling bearing a photoremovable succinimidyl carbonate*[2].

Patterned immobilization of synthetic and biological ligands on material surfaces with controlled ligand densities is important for various bioanalytical and cell biological purposes. Conventional photolithography is useful for high-resolution surface patterning, but it is not suitable for controlling ligand densities with chemically defined surfaces, due to the nonspecific photodegradation and ozone-induced damage of the surface species by deep-UV irradiation. To overcome the drawbacks of this technique, we have designed and synthesized a new silane coupling agent, which has a photocleavable 2-nitrobenzyl switch between a trimethoxysilyl group and a succinimidyl carbonate (Fig. 2a). Based on this molecular design, the compound allows for the one-step introduction of succinimidyl carbonates onto the surface of glass and silicon, immobilization of primary amines, and region-selective and dose-dependent release of the amines by *mild* near-UV irradiation (Fig. 2b). Since the photocleavage rate is almost independent on the type of amine, one can control the surface density of any amines by irradiating the substrate for an appropriate irradiation time. This compound opens up new possibilities in surface modification and patterning, not only for glass and silicon but also for inorganic oxides in general (e.g., TiO_2, Al_2O_3, Y_2O_3, and Fe_3O_4).

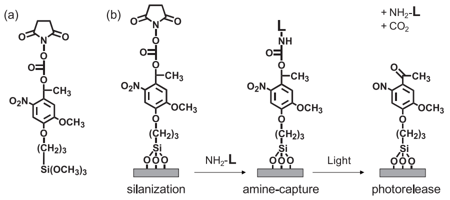

Fig. 2. (a) Chemical structure of the newly synthesized silane coupling agent and (b) schematic drawing of the immobilization and photorelease of amines on a surface functionalized with the compound.

(2) *Creation of biointerface by atmospheric plasma treatment*[3].

Plastic surfaces are often inert to chemical reactions. Plasma treatment is one way to improve the biocompatibility of plastics, but the strong power and temperature of the conventional plasma sources denature surfaces chemical species. We used non-equilibrium atmospheric low frequency plasma (LF-plasma, Fig. 3a) to conjugate poly(ethylene glycol) (PEG) monoacrylate to a polypropylene (PP) surface. To increase efficiency of the chemical linkage, we used a plasma susceptible polymer, poly(chloromethylstyrene) (PCMS), as a midlayer (Fig. 3b). The LF-plasma treatment of the PP substrates coated with PCMS and PEG monoacrylate resulted in significant change in the surface contact angle even after washing with various solvents. Furthermore, the surface showed almost complete repellency against adhesion of HeLa cells. These results mean PEG-oriented species was successfully introduced to the chemically inert hydrocarbon polymer. The present method will be useful for the surface modification of bio-devices in a wide range of applications.

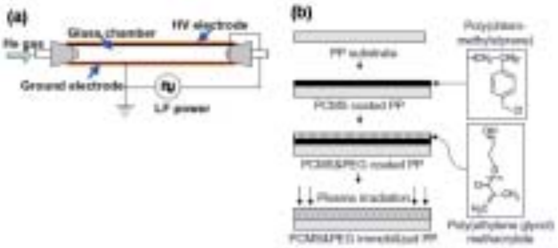

Fig. 3. (a) Schematic diagrams of low frequency dielectric barrier discharged plasma apparatus. (b) Sequential process for surface modification of polypropylene substrate by plasma irradiation.

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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.

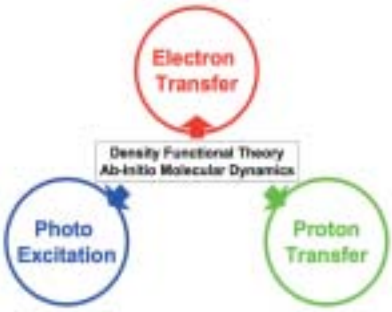

Fig. 1. **Research targets in the computational physical chemistry (Tateyama independent scientist) team in MANA.**

2. Research Activities

(1) Calculation of charge-transfer excitation energy based on time-dependent (TD) DFT linear response (LR) scheme$^{1)}$.

Nanosheets consisting of fullerene and ferrocene molecules were synthesized and found to show red-shifted excitation spectra compared to sole fullerene. In order to characterize the excitation, we have calculated the excitation energy of the possible geometry (see Fig.1 (left)) and demonstrated that the red-shift is attributed to the charge-transfer excitation from ferrocene to fullerene. Note that the treatment of charge-transfer is still challenge in the framework of TDDFT-LR scheme.

(2) Excited-states dynamics of organic molecule based on TDDFT real-time propagation (RTP) scheme$^{2)}$.

Laser flash photolysis process of diazomethane was investigated by TDDFT-RTP scheme (see Fig.1 (right)). Our simulation showed the initial stage of the rearrangement in the excited state (RIES) mechanism proposed by experiment recently, where the main structural change occurs on the singlet S_1 state.

(3) Development of all-electron calculation method of non-adiabatic coupling in the framework of TDDFT-LR scheme$^{3)}$.

Non-adiabatic coupling (NAC) is indispensible for the excited-state dynamics simulation. We have developed the all-electron scheme with local basis to calculate NAC, and found that a certain sum rule practically exists and electron correlation is sometimes crucial for better accuracy.

(4) First principles molecular dynamics (FPMD) study on interfacial water on TiO_2 anatase (101) and (001) surfaces with TiO_2 slab soaked in bulk water$^{4)}$.

We have carried out FPMD simulations at room temperature of TiO_2 anatase surfaces soaked in bulk water (see Fig.3), and given a novel classification of interfacial water molecules based on the strength of the hydrogen bonds in the trajectory.

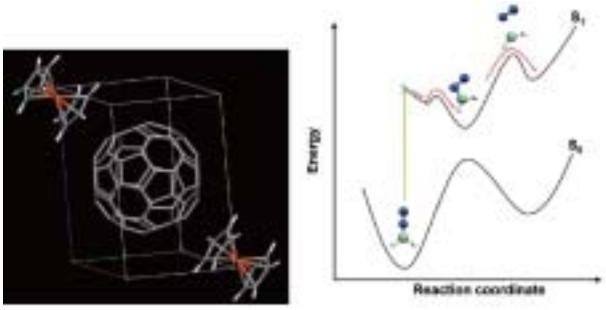

Fig. 2. **(left) Nanosheets consisting of fullerene and ferrocene showing charge-transfer spectra. (right) photolysis mechanism of diazomethane suggested by our TDDFT-RTP simulation.**

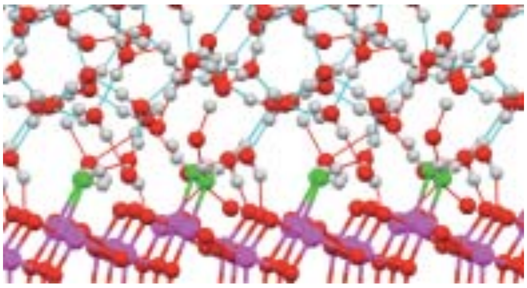

Fig. 3. **Snapshot in the equilibrium trajectory of TiO2 anatase/water interface obtained by our FPMD simulations. Several types of hydrogen bonds are found in this interfacial region.**

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Iron-Based Superconductivity

MANA Independent Scientist Shunsuke TSUDA

1. Outline of Research

For energy saving, many approaches were tested recently. One of the solutions is an application of superconductivity. As was well known, superconducting materials have no resistance at a superconducting state. Therefore, for example, when we use it for an electric power cable, huge amount of the energy consumption can be suppressed even in the present superconducting transition temperature (T_c). Needless to say, higher T_c is much more plausible.

In this decade, the world record of T_c, which is 135 K at ambient pressure in copper oxide superconductors, was not rewritten. On the other hand, while the T_c is lower than the highest one, many novel superconductors had been discovered. This means that further novel superconductors can be discovered. Actually in 2008, iron-based superconductors were discovered. Fortunately, in contrast to MgB_2, iron-based superconductors have varieties in the crystal structure. The iron-based superconductors can be categorized into several groups from structural point of view. Representative four structures were listed 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.

In this research, we studied superconducting mechanism and application of a novel superconductor, iron-based superconductor. Especially, we focused on FeSe as in the Fig. 1 (c). FeSe has the simplest structure among iron-based superconductors. Therefore, these compounds may give us an unique opportunity to understand the superconducting mechanism.

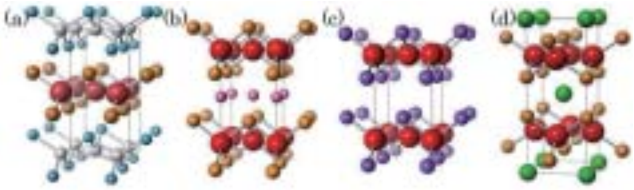

Fig. 1. Representative crystal structures of the iron based superconductors. (a) 1111 structure (b) 111 structure (c) 11 structure (d) 122 structure. (http://www.jst.go.jp/extra/2008/081031.html)

2. Research Activities

(1) Substitution effect on the electronic state of FeSe [1)]

We performed high-resolution photoemission measurements on $Fe_{1-x}M_xSe$ (M = Co, Ni) and $FeSe_{1-y}Te_y$. Co and Ni substitution increase the valence electron numbers. This indicates that the valence band should be filled by the doped electrons. On the other hand, Te substitution does not change the band filling.

The photoemission spectra in wide energy region are shown on Fig. 2. As was expected, Te substitution hardly affect on the spectrum. Co or Ni substitution induced spectral shift toward higher binding energy. This is consistent with simple band filling picture. However, the degree of the spectral shift of Co or Ni substitution with 0.05 was very similar to each other nevertheless different electron numbers of Co and Ni. At present, the origin of this anomalous behavior is attributed to electronic correlation in this system.

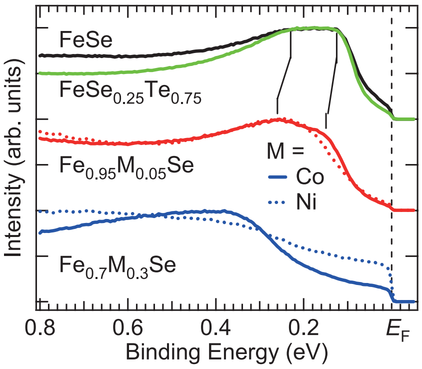

Fig. 2. Phtoemission spectra of $Fe_{1-x}M_xSe$ (M = Co or Ni) and $FeSe_{1-y}Te_y$.

(2) Fabrication of superconducting wire [2)]

To apply iron-based superconductors, we fabricated Fe(Se,Te) superconducting wire made by a method based on a power-in-tube method. Successfully fabricated wire showed superconductivity. The temperature dependence of magnetization is shown on Fig. 3. We directly obtained superconducting critical current from the wire for the first time in the world.

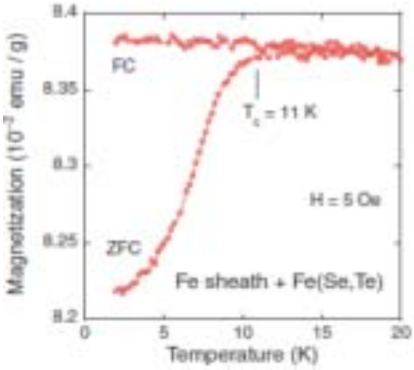

Fig. 3. Temperature dependence of magnetization for Fe(Se,Te) wire.

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

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Quantum Rods & Dots-Based Metal Oxide 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. We are developing series of novel materials for solar hydrogen generation, photovoltaics, and sensing applications utilizing low cost materials chemistry such as aqueous chemical growth to fabricate semiconductors based on quantum-confined metal oxide (hetero)-nanostructures.

2. Research Activities

We have synthesized and characterized the electronic structure and basic structural, optical, and photoelectrochemical properties of novel visible light active iron oxide-based semiconductors consisting of vertically oriented quantum rod arrays. Figure 1 shows a doped bundle of iron oxide quantum rods which by intermediate band effects enable a full visible absorption profile while still being stable against photo-corrosion for efficient and low cost solar hydrogen generation by direct water splitting at neutral pH (allowing therefore the use of low cost and abundant seawater as unique electrolyte)1).

Other low cost vertically oriented nanorod-based systems were fabricated by aqueous chemical growth for room-temperature operating gas sensors2).

Another aspect of our research activities involved the the controlled fabrication of quantum dots of tailored sizes without surfactant and thus the ability to control their surface acidity and properties. Size effect in general and quantum size effects particularly on the physical properties and electronic structure of metals and semiconductors are well established in the literature.However, the effect of quantum dot size on the chemical properties of materials and, in particular, on the surface and interfacial chemistry of hydrated metal oxides has scarcely been reported. Yet, such an effect could be of great relevance for a better fundamental understanding of structure-properties relationships as well as for important environmental and industrial applications such as heterogeneous catalysis, chemical, biological, and environmental adsorption phenomena, as well as for water purification and remediation of toxic substances. We have investigated the effect of quantum dots on the water-oxide interfacial chemistry of γ-Fe_2O_3. Theoretically, by considering the large variation of the surface curvature of very small nanoparticles compared to larger ones on the adsorption/desorption equilibrium at the water-oxide interface, a significant change in surface acidity should occur. Indeed, the effect of size on the surface chemistry of metal oxides was demonstrated (fig.2) by the reversal of the surface acidity from acidic to neutral to basic by changing the size from 12 to 7.5 to 3.5 nm, respectively3).

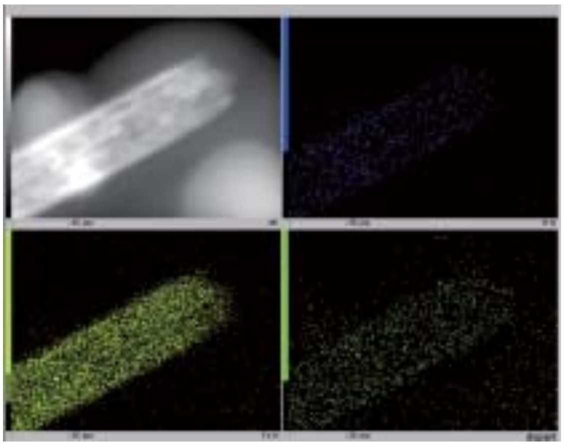

Fig. 1. High resolution transmission electron microscopy image of a doped iron oxide quantum rod bundle and corresponding energy dispersive elemental mapping analysis.

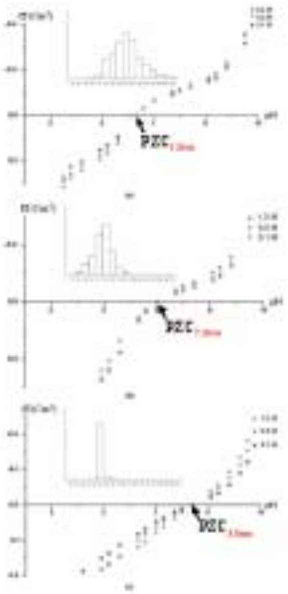

Fig. 2. Titration diagrams of aqueous suspensions of maghemite consisting of spherical nanoparticles of 12(a); 7.5(b); and 3.5 nm (c) in average diameter in $NaNO_3$ aqueous solutions of various concentrations at 25°C. The single point of intersection of the three titration curves of indicates the point-of-zero-charge (PZC). The insets show the histograms of size distributions as determined by electron microscopy.

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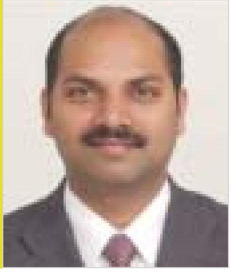
Size Controlled Fe_2O_3 Nanoparticles in Nanoporous Carbons and Silica and their Unusual Magnetic Properties

MANA Independent Scientist Ajayan VINU



1. Outline of Research

Magnetic iron oxide nanoparticles have been the interest of researchers from academic and industry because of their promising applications in data storage, electronic and biomedical devices, and magnetic carriers for drug delivery.[1)] However, many of these applications require Fe_2O_3 nanoparticles with controllable size as they exhibit interesting magnetic properties, and the fabrication of those nanoparticles is always a challenging task. Consequently, several synthetic approaches, including heating up, hot injection, sonochemical, and thermal decomposition of organometallic compounds, have been employed for the fabrication of Fe_2O_3 nanoparticles with uniform size and shape.[1)] However, most of the synthetic approaches generate large size agglomerated Fe_2O_3 nanoparticles with irregular shape, which have drawbacks such as low magnetic moment. An interesting way to finely control the particle size and shape is to encapsulate magnetic particles inside the porous inorganic template matrix with definite pore size and shapes.

Here we demonstrate for the first time a nano-sieve approach for the fabrication of the magnetic Fe_2O_3 nanoparticles with controllable size inside the nanoporous confined matrix of hexagonally ordered silica materials with tunable pore diameters (Figure 1A).[2)] We further successfully demonstrate that the particle size and the magnetic properties of the nanoparticles can easily be controlled by simply tuning the pore size of the nanoporous silica matrix. The Fe_2O_3 nanoparticles in the supports were prepared by wet impregnation method and the samples were denoted as XF-SBA-15-Z where X, F, and Z denote the weight% of the Fe_2O_3, Fe_2O_3, and the temperature used for the synthesis of SBA-15, respectively.

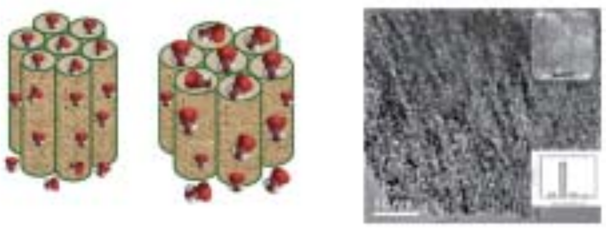


Figure 1. A) Schematic representation of the controlling the size of the Fe_2O_3 nanoparticles by simply tuning the pore size of the nanoporous silica materials. B) Representative HRTEM image of iron oxide nanoparticles in mesoporous silica template. (inset above: HRSEM image, scale bar 20 nm and below: particle size distribution).

2. Research Activities

Figure 1B shows the representative HRTEM and the related histogram of HRTEM 30F-SBA-15-130. The sample shows clearly the Fe_2O_3 nanoparticles with uniform size and shape inside the linear array of pores of SBA-15-130, which are arranged in regular intervals, confirming that the ordered pores indeed control the particle size and shape of the Fe_2O_3 nanoparticles (Figure 1B inset). It is interesting to note that the diameter of the Fe_2O_3 particles grown inside the SBA-15 nanochannels is between 6.5 to 9 nm, which is almost similar to the pore size of the SBA-15 supports and significantly smaller than that of the particles made without SBA-15. Noteworthy, the size of the Fe_2O_3 nanoparticle increases with the increase of the pore size of SBA-15.

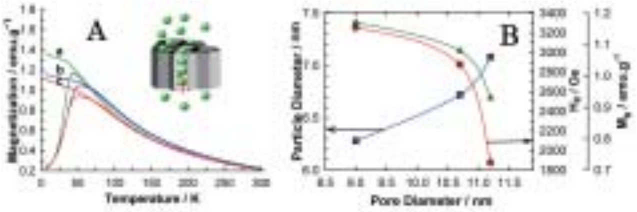


Figure 2. (A) FC and ZFC curves of (a) 30F-SBA-15-100, (b) 30F-SBA-15-130, (c) 30F-SBA-15-150; (B) The influence of pore diameter of the template on the coercivity (Hc) and the magnetization at the maxima (MB). Inset (2A) – schematic representation of Fe_2O_3 nanoparticles in SBA-15.

One of the interesting findings in the work is control of the magnetization of the nanocomposites by controlling the pore diameter of the SBA-15. Figure 2A shows the zero field cooling (ZFC) and field cooling (FC) curves measured at the magnetic field 1000 Oe for Fe_2O_3 nanoparticles grown on SBA-15 template with various pore diameters. Interestingly, it can be seen that the blocking temperature (T_B) increases with increasing the pore diameter of the SBA-15. The diameter of the Fe_2O_3 particles is calculated to be around 6.3 to 7.1 nm, which is close to the data obtained from HRTEM images. Moreover, as the pore diameter of the support decreases, the magnetization and the magnetic coercivity (Hc) increase with the concomitant decrease of the T_B due to the small particle size (Figure 2). This confirms that the size of the Fe_2O_3 can be controlled by simple adjustment of the pore diameter of the SBA-15. It must also be noted that the coercivity and the magnetic remanence vary inversely with the pore diameter of the support and the particle size of the nanoparticles (Figure 2B). This is the first time, to our knowledge that size of Fe_2O_3 nanoparticles and their magnetic properties are tuned by varying the pore diameter of the large pore SBA-15.

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Theoretical Design and Physical Properties Forecast of Nano-Carbon Electronics Devices

MANA Independent Scientist Katsunori WAKABAYASHI

1. Outline of Research

Our research target is to theoretically reveal the peculiar electronic, magnetic and transport properties in nanocarbon materials such as graphene, nano-graphene, graphene nanoribbons, nanotubes using theoretical and/or computation method. Recently graphene, a single-layer of graphite, has attracted much attention both from the fundamental and applied sciences, since the electronic states are described by the massless Dirac Fermion in sharp contrast with the conventional two-dimensional electron gas on the semiconductor devices. Such unconventional electronic states are the sources of the peculiar electronic properties of graphene, which are characterized as the half-integer quantum Hall effect, the absence of backward scattering, Klein tunneling and ultrahigh mobility of electrons.

The successive miniaturization of the graphene electronic devices inevitably demands the clarification of edge effects on the electronic structures, electronic transport and magnetic properties of nanometer-sized graphene. The presence of edges in graphene has strong implications for the low-energy spectrum of the π-electrons. There are two basic shapes of edges, armchair and zigzag, which determine the properties of graphene ribbons. It was shown that ribbons with zigzag edges (zigzag ribbon) possess localized edge states with energies close to the Fermi level. These edge states correspond to the non-bonding configurations. In contrast, edge states are completely absent for ribbons with armchair edges. Recent experiments support the evidence of edge localized states. Also, it has been recently reported by several overseas groups that graphene nanoribbons can experimentally be produced by using lithography techniques and chemical techniques.

On the background mentioned above, the main purpose of our research is to clarify the peculiar features in electronic, magnetic and transport properties of nano- and meso-scopic systems based on carbon materials. Also, we aim to design and explore theoretically the new functionalities as the next-generation devices based on the peculiar electronic properties.

2. Research Activities

(1)Perfect Conducting Channel: [1)]

Numerical calculations have been performed to elucidate unconventional electronic transport properties in disordered zigzag nanoribbons. The energy band structure of zigzag nanoribbons has two valleys that are well separated in momentum space, related to the two Dirac points of the graphene spectrum. The partial flat bands due to edge states make the imbalance between left- and right-going modes in each valley, i.e. appearance of a single chiral mode. This feature gives rise to a perfectly conducting channel in the disordered system, i.e. the average of conductance <g> converges exponentially to 1 conductance quantum per spin with increasing system length, provided impurity scattering does not connect the two valleys, as is the case for long-range impurity potentials.

(2) Graphene Edge Structure Engineering: [2)]

In graphene nanoribbon junctions, the nearly perfect transmission occurs in some junctions while the zero conductance dips due to anti-resonance appear in others. We have classified the appearance of zero conductance dips for all combinations of ribbon and junction edge structures. These transport properties do not attribute to the whole junction structure but the partial corner edge structure, which indicates that one can control the electric current simply by cutting a part of nanoribbon edge. The ribbon width is expected to be narrower than 10 nm in order to observe the zero conductance dips at room temperature.

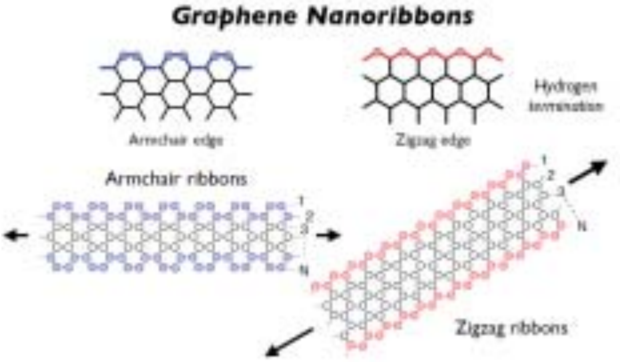

Fig. 1. Graphene nanoribbons and nanographenes show strong nanoscle and edge effect. Zigzag edge can give rise to large peak in the density of states at the Fermi energy due to the edge states.

(3) Kohn Anomalies in Graphene Nanoribbons: [3)]

The quantum corrections to the energies of the G point optical phonon modes (Kohn anomalies) in graphene nanoribbons are investigated. In relation to Raman spectroscopy, we have shown that the longitudinal modes are not Raman active near the zigzag edge, while the transverse optical modes are not Raman active near the armchair edge. These results are useful for identifying the orientation of the edge of graphene nanoribbons by G band Raman spectroscopy, as is demonstrated experimentally, in collaboration with Prof. Enoki's group at Tokyo Inst. Tech.

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Novel Optical Nano-Sensing Systems and their Applications to Biomedical Science

MANA Independent Scientist Eriko WATANABE

1. Outline of Research

The objective of my research is to develop a non-contact and non-destructive method to elucidate the biological phenomena by measuring the phase information of biological cells, at the nanoscale in real time.

In biology, most microscopy specimens, in particular living cells, are transparent and differ only slightly from their surroundings in terms of absorbance and color. Many types of bright field microscopy such as dark field microscopy, confocal microscopy, and multi photon microscopy are widely used for observation of biological activities using amplitude modulating components of light. So these methods are very difficult to detect the transparent objects. On the other hand, the phase information is modulated when it is passing through even transparent objects and is detected as phase retardation distribution. However, there still exists a serious problem regarding the signal level of the phase retardation distribution.

2. Research Activities

I first built a quantitative phase microscope in a Mach-Zehnder interferometer with full phase control and a combination of passive/active noise reduction techniques to achieve sub-nanometer sensitivity as shown in Fig.1(a). This quantitative distribution contains information concerning both morphology and refractive index of the observed specimen. As far as living cells in culture solution are concerned, it is aim at spatial resolution is diffraction-limited resolution and the optical path length accuracy is a sub-nanometer level, offering attractive possibilities for the visualization of the cellular dynamics.

Figure 1(b) is an experimental result of volume holographic grating using phase measurement system. The structure of sectional view are shown in here, the result clearly shows the periodic structure of 2.2μm interval. Spatial resolution is less than 600nm, optical path resolutions is less than 1nm. I also attempted to measure a diatom cell and Blood cell using the phase measurement system. It was scanned in two dimensions, as shown in Fig.1 (c), and we could measure the diatom cell with a spatial resolution of 600nm and axial noise level of less than 1nm.

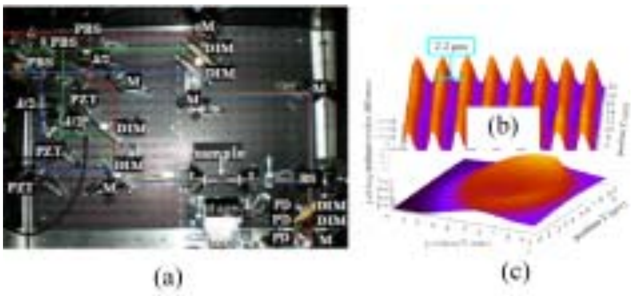

Fig. 1. (a) Phase measurement system, (b) Experimental results; Red Blood Cell , (c) Optical devices.

I secondly developed a novel correlation system for phase object using a coaxial holographic system as shown in Fig.2. I have successfully developed an entirely new concept of holographic memory system using a collinear method which is completely different from the conventional holographic memory. By preliminary correlation experiments using a holographic optical setup, I acquired extremely low equal error rates of correlation for phase objects models. Integration of the holographic disc memory and the phase measurement system enables us to achieve an automatic living cell correlation system, and this system can facilitate identifying the density and structure of the cells at very high speed.

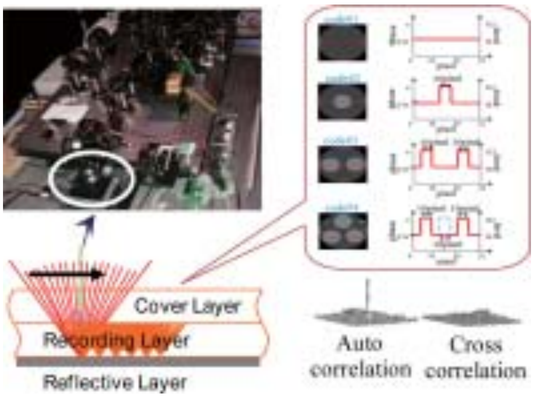

Fig. 2. A novel correlation system for phase objects.

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Advanced 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. Especially, 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.

2. Research Activities

Currently, ordered mesoporous materials prepared through the self-assembly of surfactants have attracted growing interests due to their special properties including uniform mesopores and a high specific surface area. Here we focus on fine controls of compositions, morphologies, mesochannel orientations which are important factors for design of mesoporous materials with new functionalities. Here we report our recent progress toward advanced mesoporous materials.

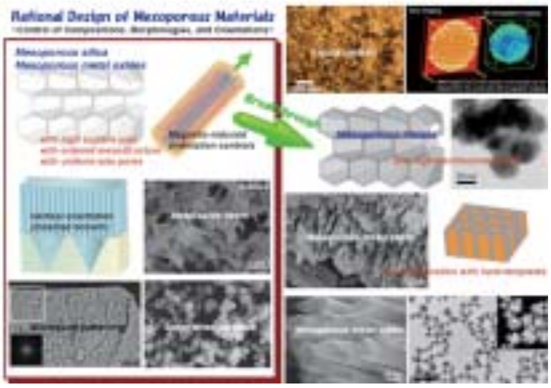

Figure 1. Fine controls of mesostructures, compositions, and morphologies toward advanced mesoporous materials.

Mesoporous materials now include a variety of inorganic-based materials, e.g., transition-metal oxides, carbons, inorganic-organic hybrid materials, polymers, and even metals. Mesoporous metals with metallic frameworks can be produced by using surfactant-based synthesis with electrochemical methods. Due to their metallic frameworks, mesoporous metals with high electroconductivity and high surface areas hold promise for a wide range of potential applications, such as electronic devices, magnetic recording media, and metal catalysts. Fabrication of mesoporous materials with controllable morphologies is also one of the main subjects in this rapidly developing research field. Mesoporous materials in the form of films, spheres, fibers, and tubes have been obtained by various synthetic processes such as evaporation-mediated direct templating (EDIT), spray-dried techniques, and collaboration with hard-templates such as porous anodic alumina and polymer membranes. Furthermore, we have developed several approaches for orientation controls of 1D mesochannels. The macroscopic-scale controls of mesochannels are important for innovative applications such as molecular-scale devices and electrodes with enhanced diffusions of guest species.

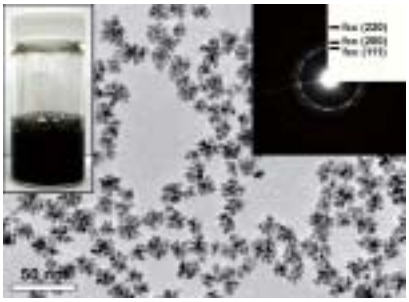

Figure 2. TEM image of nanostructured Pt nanoparticles.

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A Novel Biointerface with Well-Defined “Concentrated” Polymer Brushes Prepared by Surface-Initiated Living Radical Polymerization

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. Focusing on the unique structure and properties of the concentrated brushes, I aim to develop, by utilizing the advantages of surface-initiated LRP (SI-LRP), a concentrated brush-based novel biointerface that would precisely control biological reactions, e.g., protein adsorption, cell-adhesion, and so on.

2. Research Activities

(1) Cell Adhesion on Concentrated Polymer Brushes with different hydrophilic polymers.(2)

More recently, we demonstrated that concentrated polymer brushes of poly(2-hydroxyethyl methacrylate) (PHEMA) showed excellent protein repellency because of its unique size-exclusion effect;(3) proteins, in most cases sufficiently large compared with the distance between the nearest-neighbor graft points, are physically excluded from the concentrated brush layer and hardly adsorbed on it because of effective suppression of non-specific interaction. This notable result led me to investigate the interaction between cells and concentrated brushes, since non-specific adsorption of proteins often triggers cell adhesion. Thus I examined 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). The concentrated polymer brushes of all the three, regardless of differences in chemical structure and hydrophilicity, almost completely suppressed the adhesion of L929 fibroblast cell in contrast to the corresponding semi-dilute polymer brushes (Fig. 1).

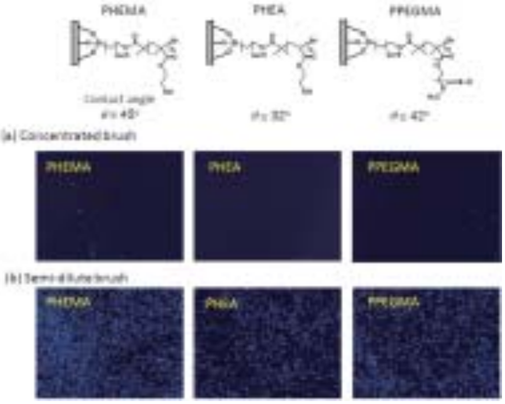

Figure 1. L929 adhesions on concentrated brushes of PHEMA, PHEA, and PPEGMA for 24 h. Incubation time = 24 h. [L929]$_0$ = 5.0×10^4 cells/cm^2. The fixed cells on a substrate were stained with Hoechst 33258 to color nuclei in blue.

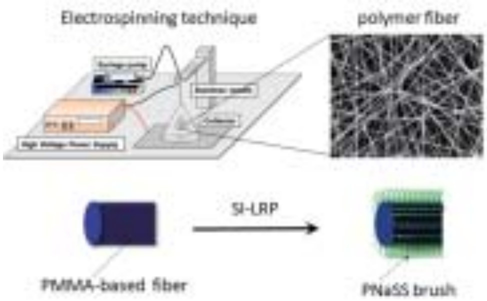

Figure 2. Surface modification of electrospun fibers by SI-LRP.

(2) Surface Modification of Electrospun Nanofibers by SI-LRP.(4)

Electrospinning technique currently has attracted much interests for their potential applications in tissue engineering, biosensor technology, drug delivery system, and so on. This technique can fabricate non woven mat and sponge form composed of fibers of various polymers with diameters ranging from a several tens nm to a few μm, yielding large surface area, tuneable chemical property, and controllable mechanical property. However, in spite of such advantages, the electrospun fibers are still far from real applications because of a poor control of surface functionality. Thus, in this work, I aimed to fabricate concentrated brushes on surfaces of electrospun fibers by SI-LRP (Fig. 2). As I mentioned above, concentrated brush obtainable by SI-LRP provides unique properties as well as excellent biointertness. By optimizing conditions of electrospinning and SI-LRP, I successfully prepared concentrated poly(styrene sodium sulfonate) (PNaSS) brushes on PMMA-based fibers by SI-LRP.

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EBIC Investigation of Stress-Induced Leakage Defects in High-k Gate Stacks

ICYS-MANA Researcher Jun CHEN

1. Outline of Research

High-k/metal gate stacks are promising structures for the future CMOS devices. Presently high-k films contain a relatively high concentration of electrically active defects compared to SiO_2. The potential instabilities or failures caused by these defects limit the introduction of high-k gate dielectrics for practical applications. Reliability studies are indispensable for understanding and using high-k devices.

Recently we have proposed an electron beam induced current (EBIC) technique for the characterization of leakage sites in high-k dielectrics.[1] This technique is quite applicable to high-k dielectrics, because their leakage and breakdown behavior is gradual compared to the abrupt breakdown of SiO_2. It is expected that breakdown sites could be revealed gradually until hard breakdown occurs. For instance, figure 1 shows the TDDB (time dependent dielectric breakdown) characteristics of a p-channel MOSFET with HfSiON gate dielectric. The breakdown device was inspected by EBIC as bright spots in the EBIC mapping. It is suggested there is a clear correlation between dielectric breakdown and EBIC sites in high-k MOS devices.

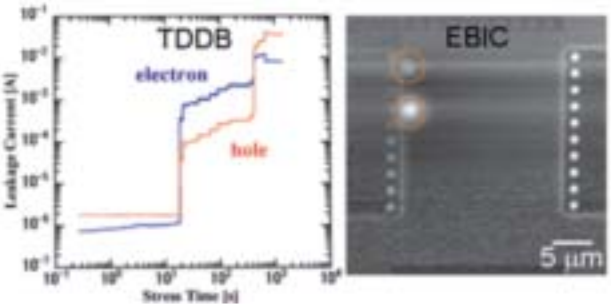

Fig. 1. TDDB current profiles of an n^+poly-Si pMOSFET under a CVS of -3.8 V and EBIC image of the TDDB tested sample at -0.1 V. The two leakage sites are believed to correspond to the two TDDB current jumps.

On the other hand, the roles of pre-existing defects and stress induced defects are very important for understanding the leakage and breakdown processes. Our recent work has found an initial higher density of leakage sites in n-well capacitors compared to p-well capacitors. With careful EBIC setup, we can observe not only the pre-existing defects but also the electrical stress induced defects, which is believed to result in SILC (stress induced leakage current). Until now there is no direct view of these defects. How do they exist and generate? What is their impact on the device failure? To address these questions we present new findings on pre-existing and stress-induced defects using EBIC with bias, time, and temperature dependencies.

2. Research Activities

(1) Pre-existing defects in various high-k gate stack[1]

Figure 2 shows the EBIC images of n-well capacitors with HfSiON gate dielectric capped with various gate electrodes. There are many bright spots in the poly-Si and TaSiN gates, while only four bright spots in the corner of TiN gate. These pre-existing defects in fresh samples are strongly dependent of the gate stack structure. It suggests that the TiN deposition process does not introduce much damage to HfSiON, while poly-Si and TaSiN deposition processes can easily introduce defects to the high-k. From this, TiN appears to be a promising gate electrode material.

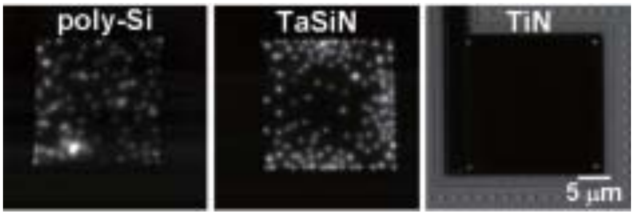

Fig. 2. EBIC images of n-well caps with different gate electrodes. Higher density of bright spots is found in the p^+poly-Si and TaSiN gates.

(2) Stress-induced defects in high-k gate stacks[2]

Figure 3 show the EBIC images of a TaSiN gate n-well capacitor taken before and after CVS (constant voltage stress). The applied CVS voltage was set at accumulation state. The initial capacitor showed a few bright spots mainly located on gate periphery. When stressed at high voltage such as 3 V for some time, many new bright spots appeared. These newly appeared spots are regarded as stress-induced defects. They exhibited a random distribution inside gate region and their numbers increased with stress time.

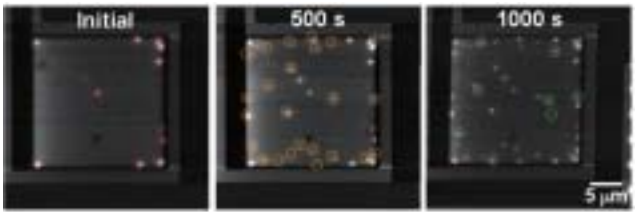

Fig. 3. EBIC images of an n-well cap before and after CVS at -3 V.

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Single-Crystalline ZnS and ZnSe Nanobelts to High-Performance Photodetectors

ICYS-MANA Researcher Xiaosheng FANG

1. Outline of Research

Semiconductor nanostructures have witnessed an explosion of interest over the last decade because of advances in their controlled synthesis and unique thermal, optoelectronic, chemical, and mechanical properties.[1] Such control and intrinsic nanostructure characteristics have enabled a design of numerous devices and integration strategies to be pursued in a rational manner. As one of the most appropriate objects for dimensionality- and size-dependent tuning of functional properties, II–VI compound semiconductor nanostructures made of ZnS and ZnSe with a wide band-gap have attracted particular attention in the past few years.

For example, with a wide band-gap of 3.72 and 3.77 eV for cubic zinc blend (ZB) and hexagonal wurtzite (WZ) forms, a diverse range of possible structures and morphologies, and superior chemical and thermal stabilities, ZnS provides a novel prospective alternative for ultraviolet (UV) detectors that would be particularly useful within the UV-A band. Being compared with all existing alternative materials, such as indirect band-gap diamond (~5.5 eV) and direct band-gap semiconductor ZnO (~3.4 eV), ZnS has a higher potential as a UV detector in this specific wavelength regime.

Zinc selenide (ZnSe), one of an important II–VI compound semiconductors with a wide direct band-gap of ~2.70 eV (~460 nm) at room temperature (RT), has long been considered as a prospective material for optoelectronic devices. ZnSe is used in II–VI light-emitting diodes (LEDs) and diode lasers working in the blue-light region. As compared to Si and GaAs, ZnSe is more sensitive to blue/UV light.

In view of their high surface-to-volume ratio (SVR) and rationally designed surface and their particular position in the field of photodetectors, we are aim to develop an effective method to high-performance ZnS and ZnSe nanostructures based photodetectors.

2. Research Activities

(1) Single-crystalline ZnS nanobelts as UV-light sensors.[2]

We have demonstrated an effective approach for the synthesis of single-crystalline ZnS nanobelts possessing sharp UV-light emission at RT via right selection of source materials and by controlling their evaporation and agglomeration rates. Individual-ZnS- nanobelt-based UV-light and multiple-ZnS- nanobelts-based sensors were successfully fabricated, and showed high potential as visible-light-blind UV-light photodetectors and ultrafast optoelectronic switches. The sensor characteristics, including a spectral response, I–V curves under various light illuminations, and time response were studied. The photoresponsivity of ZnS-nanobelt-based UV-light sensors exhibited over three orders of magnitude gain under UV-light illumination as compared to visible light. The high spectral selectivity combined with high photosensitivity and fast response time (< 0.3 s) render the present single-crystalline ZnS nanobelts particularly valuable for new ''visible-light-blind'' UV-light photodetectors, especially in the UV-A region (Fig.1).

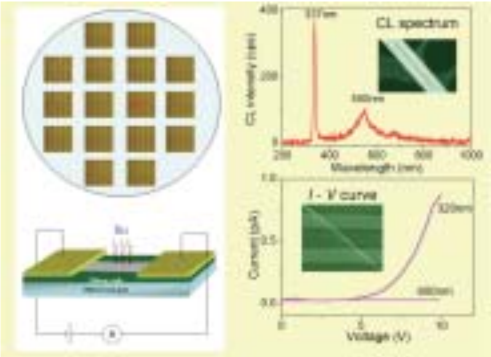

Fig. 1. Single-crystalline ZnS nanobelts as UV-light sensors.

(2) High-performance blue/ultraviolet light-sensitive ZnSe nanobelt photodetectors.[3]

We present a facile and original strategy for the preparation of ultralong ZnSe nanobelts via the en-assisted ternary solution technique. First, precursor ZnSe·3en nanobelts have been successfully fabricated. Single-crystalline-ZnSe nanobelts were then synthesized by annealing of such precursors in pure argon atmosphere at 500 ºC for 2 h. To the best of our knowledge, this is the first report on the preparation of ultralong ZnSe nanobelts via a simple solution-based route. This kind of ultralong, easily tuned/manipulated ZnSe nanobelts is valuable for nanoscale devices. Individual ZnSe-nanobelt photodetectors were then fabricated and characterized. These showed a high potential as blue/UV-light-sensitive photodetectors and ultrafast optoelectronic switches. In particular, the devices revealed an ultralow dark current (below the detection limit, 10^{-14} A, of the current meter), a high photocurrent immediate decay ratio (> 99%), and a fast time response (< 0.3 s) justifying the effective utilization of the ZnSe nanobelts as practical blue/UV-light-sensitive photodetectors (λ< 460 nm) (Fig.2).

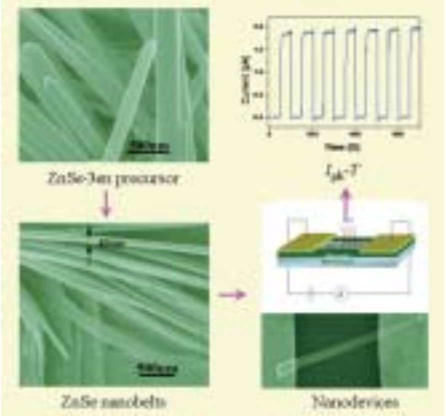

Fig. 2. ZnSe nanobelts based photodetecotors.

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Novel Functional Nanowires inside Carbon Nanotube

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

1. Outline of Research

During the last two decades, the discovery of CNTs has been followed by intense research leading this field to continuous evolution. CNTs have emerged as an attractive candidate in diverse technological applications, such as in polymer composites, sensors, and several others. An interesting aspect of the CNTs is their inner cavity which can be filled with another material in order to create novel hetero-structured nanomaterials. Importantly these are a unique class of materials having extremely large interface areas. Otherwise too, it is possible to use CNTs as a storage medium for air- or moisture-sensitive materials. Led by such motivations, the prospect to fill their inner cavities with fullerenes, metals, fluids and bio-molecules has been extensively investigated. The filling procedure is based on two methods, (a) wet chemical methods, where chemicals dissolved in solvent are used as precursors and (b) physical methods, where tip-open CNTs are infiltrated with molten materials. However, a major drawback for these techniques is that they cannot be used for many important functional materials (semiconducting ZnO or even ceramics, for instance) since these are insoluble in solvents and become reactive at higher temperatures. Moreover, the filling obtained by these conventional techniques are often partial and polycrystalline.

We are interested to develop a universal synthetic strategy to create such novel nanostructures wherein carbon nanotubes are filled with a host of functional inorganic materials, such as metals, semiconductors, insulators and heterojunctions. In particular, we are interested in obtaining single-crystalline filling.

Due to the large interfacial area, these may harbor unexpected properties and therefore we also aim to investigate each material individually, based on their possible uniqueness.

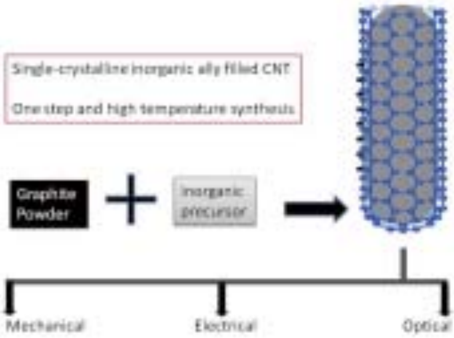

Fig. 1. Illustrative scheme of the research proposal describing synthesis of inorganically filled CNTs and relevant characterization.

2. Research Activities

(1) Synthesisof ZnS filled carbon nanotube [1]:

High temperature induction furnace was used to obtain CNTs filled with single crystalline ZnS nanowires (Fig. 2). Herein, graphite powder reacted with ZnS forming these exotic materials. The shell CNTs are turbostratic, while its diameter and thickness is tunable. The mechanical strength of the CNTs was found to increase manifold due to filling, while conductivity remained unaltered. Experiments carried out on single nanostructure showed that removal of the carbon shell from the otherwise 'black' materials exposes the ZnS core which become optical luminescent.

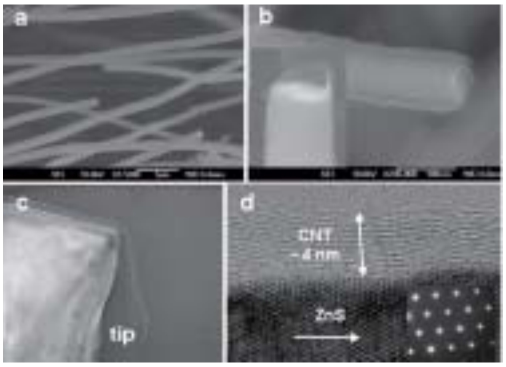

Fig. 2. (a, b, c) (a) SEM image of the core-shell nanostructures, (d) HRTEM image depicting the crystalline core and graphitic shell structure. Inset is the SAED image.

(2) Synthesis of Superconducting In nanowires and In-ZnS heterojunctions inside CNT [2]

We have synthesized single crystalline encapsulated In nanowires for the first time in a similar fashion, that can retain superconducting behavior akin to its bulk counterpart even when as small as 40 nm in diameter (Fig. 3). This was further extended to obtain ZnS-In heterojunctions, a potential semiconductor- superconductor heterojunctions inside carbon nanotube.

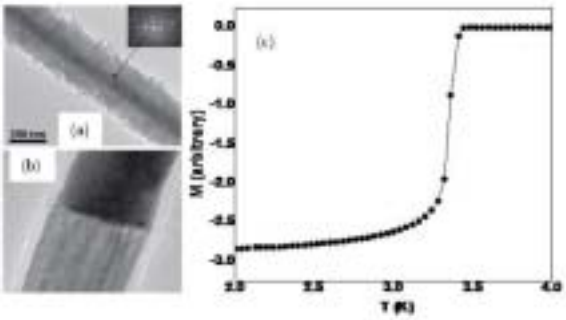

Fig. 3. TEM images of (a) Encapsulated In nanowire. (b) In-ZnS heterostructure inside CNT and (c) M-T curve for In nanowires.

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Structure Analysis of Quasicrystals and Approximants in the *RE*-Mg-Cd Systems

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

1. Outline of Research

Quasicrystals (QCs) possess long-range order and yet they lack periodicity. With their discovery it was clear that periodicity is not the only form of long-range order and the very definition of crystal had to be altered in order to take these exotic materials into account. Because of their aperiodic long-range order, the determination of the atomic structures of quasicrystals still remains one of the most challenging tasks. Approximants (APs) are “conventional” crystals in the sense that they are periodic and their structures can be defined by the atomic decoration of a 3D unit cell. However, they are related to quasicrystals by containing similar atomic clusters as do their related QCs. Therefore APs can provide crucial information concerning local atomic decorations and chemical order that later can be used for modeling the structures of related QCs. In this work we have investigated the atomic structures of several ternary phases in the *RE*-Mg-Cd systems (*RE* = Pr, Y, Yb) which are related to the binary icosahedral quasicrystal in the Yb-Cd system. Recently a complete structure model was obtained for this binary $YbCd_{5.7}$ quasicrystal[1)] which was verified by structure refinement. However binary quasicrystals are very rare and thus one of the aims of this project is to expand this binary structure model to encompass related ternary phases. When a third element such as Mg is introduced into the *RE*-Cd system, partial chemical mixing will occur between Mg and Cd. We must thus in addition to determining atomic positions also determine the distribution of chemical species in the crystals. Structure refinements on approximant phases with varying Mg-content have been performed in the Pr-Mg-Cd and Y-Mg-Cd systems. The obtained information concerning structure and chemical order between Mg and Cd in these approximants has been used to correctly interpret the structure of the ternary QC in the Yb-Mg-Cd system. The structure refinement on this quasicrystal with the composition Yb12Mg52Cd36 indicates that it has similar atomic clusters and chemical order as do the investigated approximants as seen in Figs. 1 and 2.[2)]

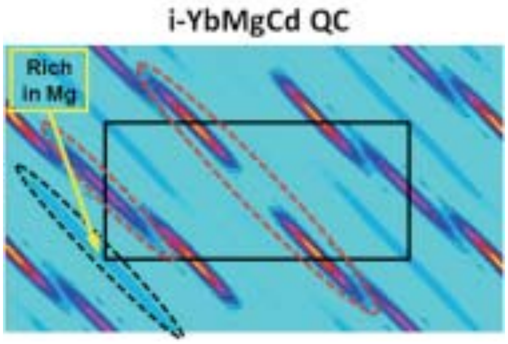

Fig. 1. Electron density map of $Yb_{12}Mg_{52}Cd_{36}$ quasicrystal showing a 2D section of the 6D unit cell. The Occupation Domain at the vertex is rich in Mg resulting in a low electron density.

2. Research Activities

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

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. Fig. 2. Shows the similarity in chemical order between the approximant in the Y-Mg-Cd system and the Yb-Mg-Cd quasicrystal. The electron density maps and chemical mixing ratios were obtained through structure refinements on both approximant and quasicrystal.

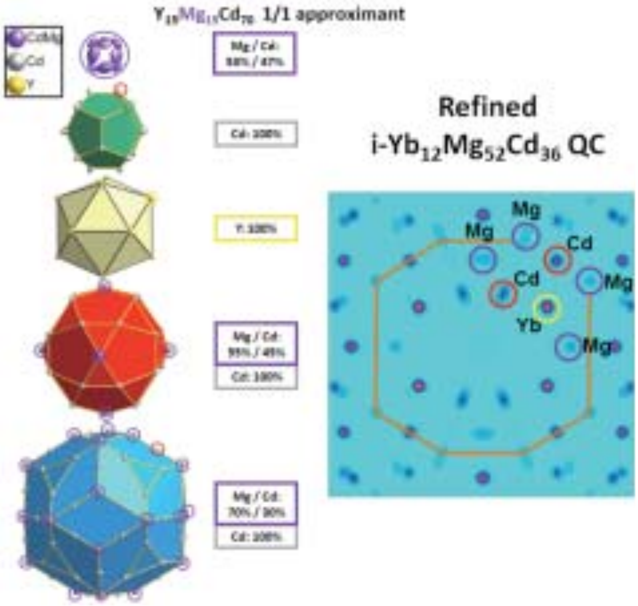

Fig. 2. Refinement results showing the similarity between *RE*-Mg-Cd approximants and quasicrystals in cluster structure and distribution of elements in the different shells of the atomic cluster.

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Hexagonal AlN Growth on Cubic Diamond Substrates

ICYS-MANA Researcher **Masataka IMURA**

1. Outline of Research

The target materials are III-nitrides and diamond semiconductors, and the research interest is their combination. In this study, I will challenge to prepare the AlN / diamond heterostructure. The aim is to develop the high-electron mobility transistor (HEMT) and optical devices (light emitting diode and photo diode) by using such the heterostructure.

In this study, I propose AlN / diamond heteropitaxial structure to overcome these problems and develop the frontier optoelectronic devices. The final target is the realization of optical devices (light emitting diode and photo diode). First, the establishment of AlN / diamond heteroepitaxal growth is required. Hence, AlN layers are grown on diamond substrates by metal-organic vapor phase epitaxy (MOVPE), subsequently, the structural quality of layers are analyzed by mainly X-ray diffractometry (XRD) and transmission electron microscopy (TEM), which feed back for crystal growth to optimize the growth condition. Then, I develop the two themes such as HEMT and optical devices.

As the first step, undoped AlN layers were grown on the (001) and (111) Ib-diamond substrates in a hydrogen flow by high-temperature MOVPE. Trimethylaluminum (TMAl) and ammonia (NH_3) were used as the Al and N sources, respectively. The thermal cleaning of the substrate was performed at 1270 °C in hydrogen atmosphere for 5 min, and then AlN layers with 1.6 µm thick were grown. The reactor pressure was kept at 133×102 Pa during growth. The V/III ratio was fixed at 116, and the corresponding amount of TMAl and NH_3 flows were 40 µmol/min and 0.1 l/min, respectively.

2. Research Activities

(1) AlN growth on (001) diamond substrates [1,2]

Figure 1 shows a bright-field cross-sectional TEM image of the AlN layer on (001) diamond substrate. The TEM image was taken under the [110] diamond zone-axis condition. The AlN grains close to the interface show a polycrystalline pattern by selected area electron diffraction (SAD). Analysis of the SAD patterns of AlN grains at different locations close to the interface regions revealed that most of AlN grains grew randomly. The XRD results indicated that these randomly oriented AlN grains comprise $(1\bar{1}01)$ and $(1\bar{1}02)$ AlN grains. However, in the upper and middle regions, the AlN layer had a wurtzite structure and was composed of c-axis-oriented grains with either $[11\bar{2}0]$AlN or $[1\bar{1}00]$ AlN. The growth mechanism governed by the higher growth rate of the AlN grains along the [0001] direction than along other directions at high growth temperatures up to 1270 °C.

(2) AlN growth on (111) diamond substrates [3]

Figure 2 shows a bright-field cross-sectional TEM image of the AlN layer on (111) diamond substrate. The TEM image was taken under the $[1\bar{1}0]$ diamond zone-axis condition. The SAD pattern analysis for the different locations in AlN revealed that a randomly oriented SAD pattern of AlN was not observed. $[1\bar{1}00]$ AlN was aligned to $[1\bar{1}0]$ diamond in the upper and middle regions. In addition, (0001)$[1\bar{1}00$AlN is predominantly aligned on (111)$[1\bar{1}0]$diamond, while (0001)$[11\bar{2}0]$AlN is partly aligned on (111)$[1\bar{1}0]$diamond. Thus, the predominant orientation was found to be (0001)$[1\bar{1}00]$AlN || (111)$[1\bar{1}0]$diamond, and the orientation was considered to be suitable for AlN growth on a (111) diamond substrate. The growth dynamics is significantly different from that of the AlN layer grown on (111) Si. The growth mechanism is understood by considering periodic atomic arrangement of the AlN and (111) diamond.

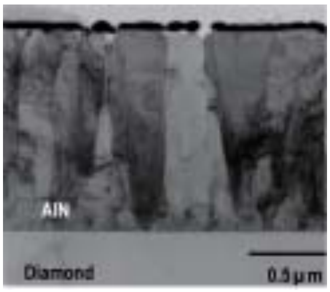

Fig. 1. XTEM of AlN on (001) diamond substrate.

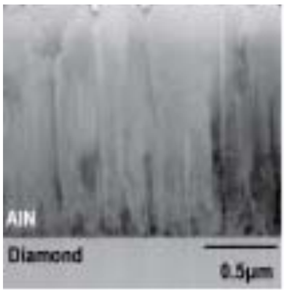

Fig. 2. XTEM of AlN on (111) diamond substrate.

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Nanoscale Self-Assembly on Surfaces

ICYS-MANA Researcher Michael V. LEE

1. Outline of Research

Self-assembly on surfaces requires control on multiple levels. Each surface has unique electrical, magnetic, thermal, chemical, physical, and functional properties that can be altered drastically even with simple processing. Molecules can be anchored to a substrate with covalent, polar, nonpolar, ionic, or hydrogen bonding and can be reversible or irreversible. Interactions between molecules can be mediated by these same forces. I focus on binding organic molecules or polymers to conducting and semiconducting surfaces. That connection at the interface is the foundation of any subsequent structure.

By combining state-of-the art surface analysis and high-level ab-initio calculations, I can understand the mechanism and choose the desired binding. With the right polymers a surface pattern can be grown into the third dimension without losing pattern fidelity until external forces are applied to change the growth pattern. Other interchangeable polymers allow different structures to be grown. This is illustrated in Figure 1.

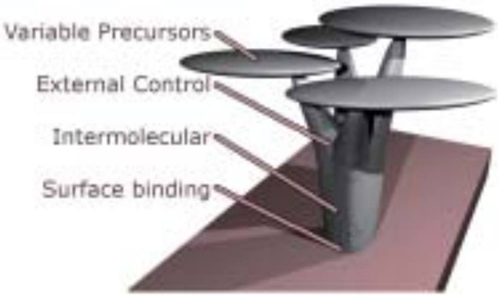

Figure 1. Depiction of the different factors that can be used to control nanoscale organic surface structure growth.

2. Research Activities

(1) Covalent Self-Assembled Monolayers

The thin outer shell of any object often has significantly different properties than the bulk. Even though these surface layers are on sometimes as thin as or thinner than one nanometer, they have a dramatic influence on effective properties because they interface or connect the bulk to the outside world. As fabrication moves to tens of nanometers and below, the interface volume becomes greater than the bulk, amplifying its effects.

Using synchrotron NEXAFS analysis, we probed the covalent bonds that control the assembly of these monolayers and discovered significant double bonds (Figure 2).$^{1)}$ In the future, NEXAFS analysis may explain the differences seen in monolayers that were previously unexplainable and lend better control over their self-assembly. Using the knowledge gained from NEXAFS, we were able to select a desired binding and make an ordered monolayer on an intrinsically rough surface.

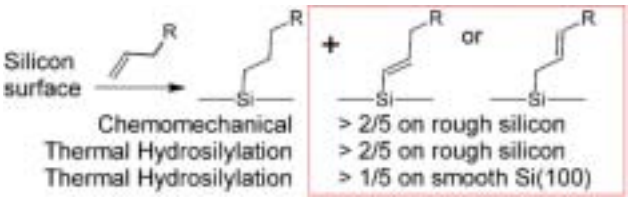

Figure 2. Two different methods of forming the simplest covalent organic monolayers directly on silicon showed.

(2) Self-Replicating Polymer Structure

Although it seems to be difficult to control, we have synthesized some monolayers that are able to replicate a surface pattern and create polymer structures with aspect ratios of over 100:1.

(3) Hexagonal Pattern Induced by External Control

Additional control over polymer assembly requires understanding the response of a specific polymer to varying conditions. By controlling conditions during solvent evaporation, we were able to form regular hexagonal patterns of holes over a large area in a polymer film (Figure 3). Simple spin-coating on a substrate was used to deposit the layer. We were also able to show that the film floats on the top of the solution, pulling polymer out of solution rather than sinking in.$^{2)}$

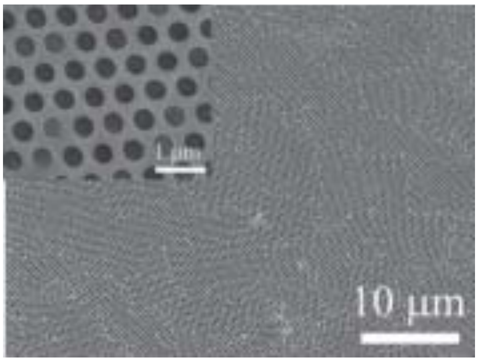

Figure 3. Macroscale array of uniform holes in polymer film. Inset shows close up image of the same holes pattern.

(4) Interchangeable Polymer Building Blocks

We developed a series of monomers with the same polymerization mechanism. This allows variation in the surface functionality and self-assembly without affecting the basic polymer growth. This allows integration with other kinds of polymerizations.

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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) Phase decoupling of charge-density waves and Periodic Lattice distortion

Low-density Pure 1D metals generally undergo a temperature-introduced Peierls transition, which leads to the formation of charge-density waves (CDW) accompanied by a periodic lattice distortion (PLD). The CDW and the PLD have the same periodicity and correlated phases through an electron-phonon coupling. By introducing small number of Co atoms as impurity into a CDW system, the Si(111)-4x1-In surface, we found that the CDW phase is decoupled from the PLD due to the phase pinning of the impurities.

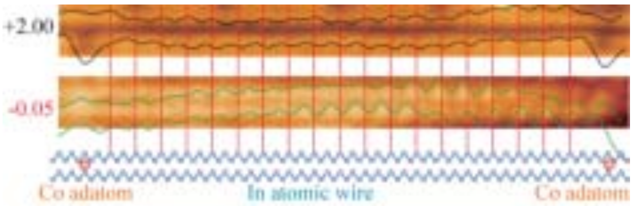

Fig. 2. Two STM images of In atomic wires with two Co atoms adsorbed thereon, as illustrated in the lower schema. Superimposed curves show the periodic modulation, which corresponds to PLD (+2.00 V) and CDW (-0.05 V) of the In atomic wires. Difference in the modulation between +2.00 V and -0.05 V imply the decoupling of PLD and CDW.

(2) Coexistence of gapped and gapless CDW observed in indium atomic wires with Co adatoms.

An array of In atomic wires, the Si(111)-4×1-In surface, condensates to a CDW state with an energy gap at EF when being cooled below ~120 K. By depositing Co adatoms on the In atomic wires and cooling them to 79 K, we found with STM that the indium wires have two domains: (8×2) domain with an energy gap at EF and ("4×2") domain without the energy gap, indicating the coexistence of gapped and gapless CDW.

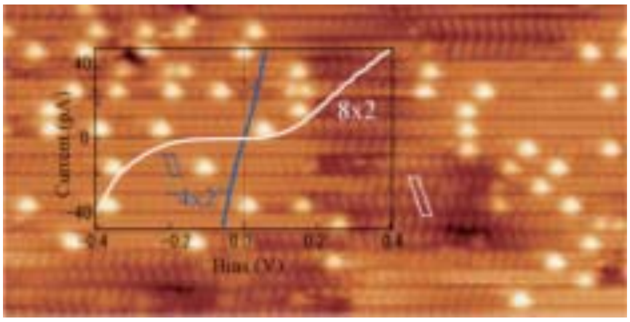

Fig. 3. STM images of Co adsorbed Si(111)-4×1-In surface. Big and small parallelograms indicate (8×2) and ("4×2") domains, respectively. Superimposed I-V curves are taken on these two domains: (8×2) curve shows a semiconducting while ("4×2") a metallic behavior.

Catalytic Microbots for the Transport, Delivery and Assembly of Microobjects

ICYS-MANA Researcher Samuel SANCHEZ

1. Outline of Research

Natural motor proteins, "bionanorobots," have inspired researchers to develop artificial nanomachines (nanorobots) able to move autonomously by the conversion of chemical to mechanical energy. Such artificial nanorobots are self-propelled by the electrochemical decomposition of the fuel (up to now, hydrogen peroxide). One of the major challenges is to achieve autonomous movements of micro- and nanoscale machines in a fluid and employ them to perform complex tasks such as drug delivery, transport and assembly of micro-/nanoobjects[1]. Richard Feynman in his 1959 speech "There's Plenty of Room at the Bottom" envisioned microscopic factories with tiny machines which could perform sophisticated tasks. Catalytic synthetic micro- and nanomotors are of growing interest because of their high locomotive power and easy control. The transport of spherical particles used as cargoes was recently achieved by either using electrostatic or chemical interactions as well as magnetic interactions. Up to now, these nanorobots are not powerful enough to deliver "large" particles.

The aim of this project is to develop a fully wireless motion controlled micro/nanorobot with enhanced properties compared with recent published ones. We explored different structures and different synthetic method of fabrication of nano/microbots. Therefore, three sub-projects were carried out.

(i) Electrodeposition of metals to fabricate bimetallic nanorods. In addition to metal deposition, conducting polymer was electrodeposited to fabricate hybrid structures.
(ii) Chemical vapor reduction which allowed us to tune from rod to tube structures,
(iii) Photolithography and Electron Beam Deposition of metals to roll-up thin films into microtubular structures.

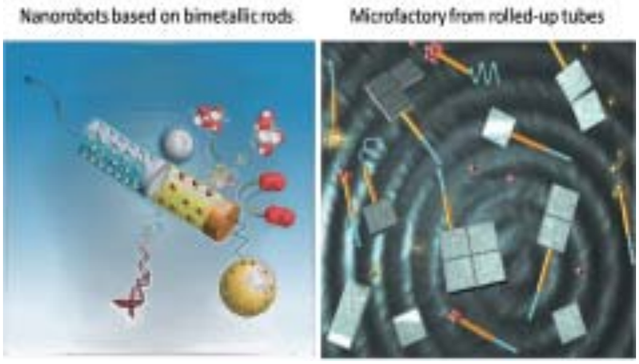

Fig. 1. Schematic drawing of the two different Nanorobots systems developed. Left: Bimetallic rod shape with possible functionalizations. Right: Microfactory using rolled-up tubes from thin films to transport and deliver microobjects.

2. Research Activities

(1) Synthesis of catalytic nanostructures by chemical vapor deposition and electrochemical deposition.

Two synthetic methods were used in combination with anodic alumina templates: i) Chemical reduction of $PtCl_4$ precursor at controlled temperature to fabricate metallic nanorods which can be tuned to tubes by changing the reduction time (Fig.2, left); ii) Electrochemical deposition of different metals (e.g. Au, Ni, Pt, Ag) to be used as "chassis" for electrocatalytic nanorobots (Fig.2, right). New hybrid structures were fabricated by consequently depositing conducting polymer.

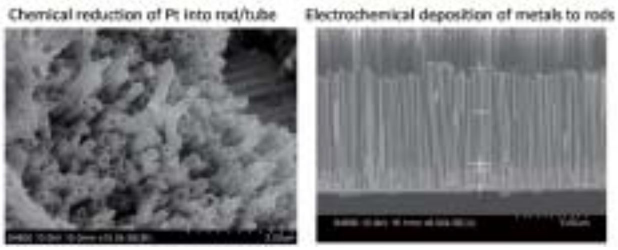

Fig. 2. SEM images of fabricated nanostructures: Pt nanotubes (left) and Au-Ni nanorods.

(2) Wireless control of tubular catalytic microbots for transport and assembly of microobjects.

We have fully controlled self-propelled catalytic Ti/Fe/Pt rolled-up microtubes (microbots) which are used to perform various tasks such as selectively loading, transport and delivery of microscale objects (microparticles, nanoplates and cells). The high propulsion power allows transporting up to 60 microparticles of 5 µm diameter and the microbots describe a force of 3.77 pN. Microbots self-propel by ejecting microbubbles via platinum catalytic decomposition of hydrogen peroxide into oxygen and water. The Fe film integrated into the tube allows the motion control by using an external magnet[2].

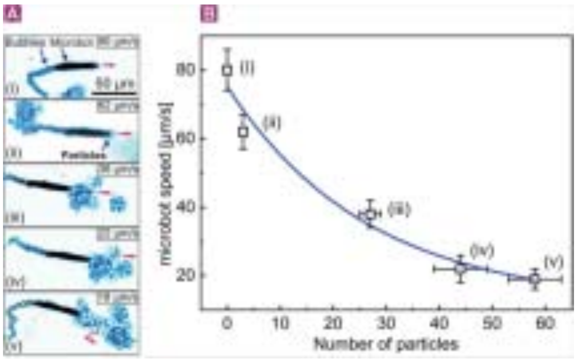

Fig. 3. (A) Transport of polystyrene microparticles of 5 um diameter. Optical microscope images of microbot loading and transporting 3 (ii), 27 (iii), 44 (iv) and 58 (v) particles. Insets show microbot's average speeds. B) Plot depicts the speed of microbots with loaded number of particles.

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Development of Novel Surface Modification using Two-Dimensional Nanosheets for Thin Film Deposition

ICYS-MANA Researcher **Tatsuo SHIBATA**

1. Outline of Research

How to control a film growth? This is one of the most important issues in thin film fabrication field used to produce various devices which underpin today's information-intensive society. Most functional materials are in crystal form. Therefore, to attain higher functionality and performance, well-controlled film fabrication of these materials is strongly desired, and many studies have attempted to achieve this. Single crystal substrates are known to be ideal substrates due to their well-defined surface atomic arrangements, which enable sophisticated control of film growth. However, single crystals have some serious limitations and disadvantages (cost, size, workability etc.). On the other hand, commonly used substrates such as glasses, metals and plastics generally lack feasible surfaces for film deposition. Accordingly, if the surface of single crystals could be copied onto such substrates, thin film technology might progress dramatically.

In this research, I plan to develop a novel way to design and control the growth of crystal films. The concept of this research is as follows: modify the substrate surface by attaching typical two-dimensional (2D) crystals named nanosheets like nano-scale wallpaper to tailor their surface patterns freely.(Fig. 1) The nanosheets are synthesized by delamination of layered host materials into colloidal single sheets via a soft-chemical procedure, and they inherit the high crystallinity of the layered precursors. Recently, I found that typical 2D surface of nanosheets could promote controlled nucleation and consequently oriented film growth on it. In other words, the nanosheets have great potential to lead and control the growing process of various crystals. The aim of this research is to establish the versatile technique using this unique nanosheet seed layer for fabricating well-crystallized and orientation-controlled functional films on various substrates such as glass and plastics.

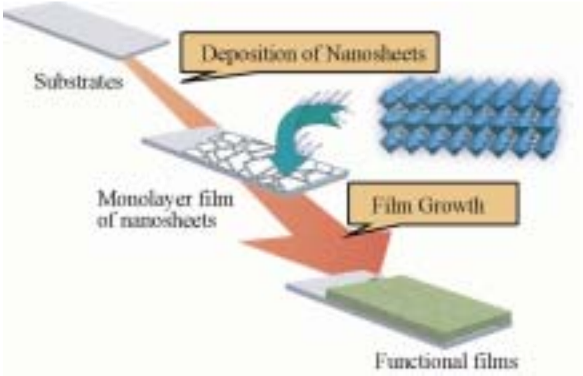

Fig. 1. Schematic explanation of nanosheet seed layer method.

2. Research Activities

(1) Room-temperature deposition of high-quality ZnO thin film on plastic substrate

Using the nanosheet seed layer method, a 2D-hexagonal structured seed layer was introduced onto glass and flexible plastic substrates via a simple solution-based deposition. High quality (001)-oriented ZnO films were grown on the $Cs_4W_{11}O_{36}$ nanosheet seed layer at room temperature by pulsed laser deposition (PLD). Highly crystalline texture directly formed on top of the substrates has been realized for the first time.(Fig. 2) Drastic improvement of film performance was successfully demonstrated by measuring the electrical conductivity of the films.

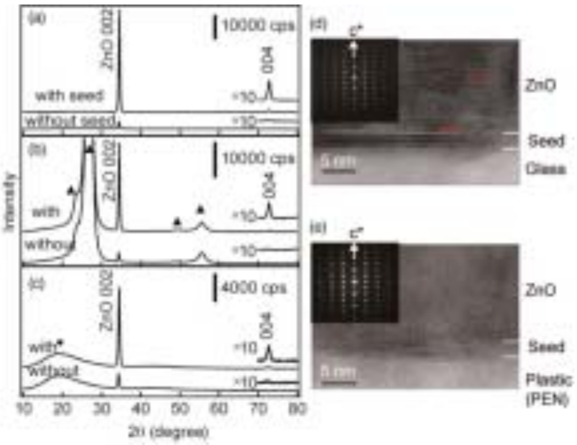

Fig. 2. XRD patterns for ZnO thin films deposited on (a) glass, (b) PEN, and (c) PET substrates. (d) and (e) Cross-sectional TEM images of ZnO films with the nanosheet seed layer.

(2) High-quality orientation controlled film growth of anatase-TiO$_2$ on glass substrate

Using a perovskite-related nanosheet ($Ca_2Nb_3O_{10}$ nanosheet), notably high-quality film growth of (001)-oriented anatase has been achieved on glass for the first time. An artificial single-crystal-like structure with the thickness of only about 1 nm was introduced just by tiling the nanosheets. The quality of the film is almost comparable to that on the well-established single-crystal substrate. Moreover, at a nanoscopic level, the epitaxial relationship between the anatase layer and the underlying single nanosheet structure was clearly confirmed.(Fig. 3)

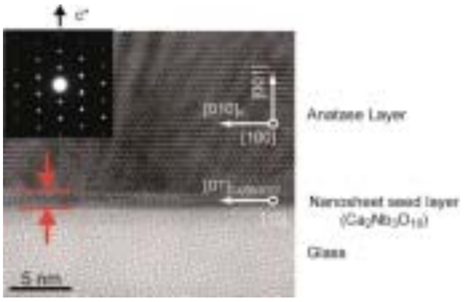

Fig. 3. Cross-sectional TEM image of TiO$_2$ thin film deposited on glass substrate with the nanosheet seed layer taken from the anatase [100] direction.

Synthesis of Nanostructured Organic Materials for Molecular Electronics

ICYS-MANA Researcher Yasuhiro SHIRAI

1. Outline of Research

The scope of the research is the development of nanostructured organic materials giving novel and unique properties, with which we can possibly realize flexible, ultra-dense, efficient, cost-effective, and/or environmentally friendly electronic and optoelectronic devices. Organic materials possess a wide range of physical and chemical properties that make them attractive candidates for realizing those devices. Radical approaches to materials fabrication and device design is, however, needed to realize fully the potential offered by organic materials. The key is the reduction of the materials fabrication and design dimensions to molecular scale. We achieved the molecular scale materials fabrication and device design using the nano-sized porous alumina template.

Design, synthesis, and application of conjugated molecules have received great attention since the suggestion of the miniaturization of electronic circuits to a molecular scale. A variety of molecules have been synthesized, and the characterization of these nanoscale electronic wires have shown promising results such as in solar harvesting devices and other optoelectronic systems. Early approaches to molecular electronics using oligo (phenylene ethynylene) OPE monolayer devices gained attention after the successful demonstration of switching effects using this class of compounds. To further advance the development of OPE-based monolayers, we have investigated fullerene-OPE hybrid devices (Fig. 1).

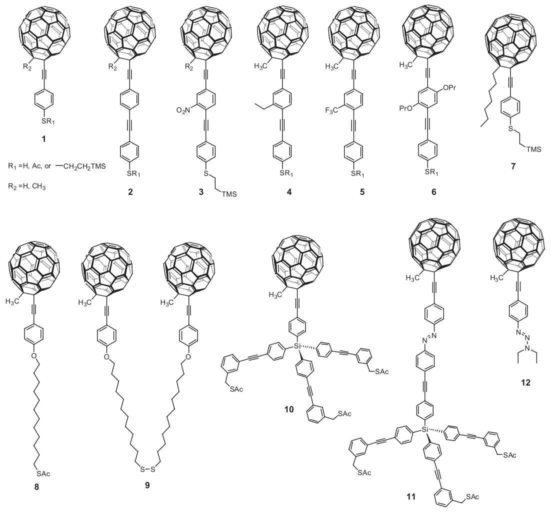

Fig. 1. Fullerene-terminated molecular wires.

2. Research Activities

(1) Synthesis and characterization of Fullerene-terminated molecular wires[1)]

A series of fullerene-terminated oligo (phenylene ethynylene) (OPEs) (Fig.1) have been synthesized for potential use in electronic or optoelectronic devices. Electronic properties such as the energy levels and the distribution of HOMOs and LUMOs of fullerene-terminated OPEs have been calculated using ab initio method at the B3LYP/6-31G(d) level. The calculations have revealed the concentration of frontier orbitals on the fullerene cage and a narrow distribution of HOMO-LUMO energy gaps. Ultraviolet photoelectron spectroscopy and inverse photoemission spectroscopy studies have been performed to further examine the electronic properties of the fullerene-terminated OPEs on gold surfaces. The obtained broad photoelectron spectra suggest that there are strong intermolecular interactions in the fullerene self-assembled monolayers, and the small band-gap (~1.5 eV), determined by the photoelectron spectroscopy, indicates the unique nature of the fullerene-terminated OPEs in which the C_{60} moiety can be connected to the Au surface through the conjugated OPE backbone.

(2) Investigation of mechanism for the conductivity enhancement in the PEDOT Nano-wires

Possibility of controlling morphology of polymer chains in conductive polymeric materials has been explored, and PEDOT was synthesized as nanowires using porous alumina templates. We have found that the template size will affect the resistivity of resulting nanowires. The nanowire gets the smaller in diameter, the more its conductivity is enhanced. To understand the mechanism for this conductivity dependence on the template size, we have explored the extent of the doping and structural properties of nanowires using XPS, EDX, and Raman spectroscopy. Both XPS and EDX analysis revealed that the extent of the doping is the same for all the nanowires with different diameters. Raman spectroscopy, however, clearly indicated the improvement in the conjugation length in the nanowires with smaller diameters. From these evidences, we can possibly suggest the carrier mobility enhancement in the polymeric materials synthesized in the nano-sized templates because the material conductivity is proportional to the product of the doping density and the carrier mobility. Organic materials with high carrier mobility are much needed in order to realize low-cost, large-area, and flexible devices. Our synthesis methodology using the porous alumina template will provide a practical route for synthesizing polymeric materials suitable for plastic electronics.

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Nanoporous Material: An Efficient Material for Fuel Cells and Drug Delivery Systems

ICYS-MANA Researcher **Pavuluri SRINIVASU**

1. Outline of Research

Ordered nanoporous 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 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.

The results indicate that the carbon source with a small molecular size is critical to achieve the nanoporous carbon materials with excellent textural characteristics. It was observed 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.

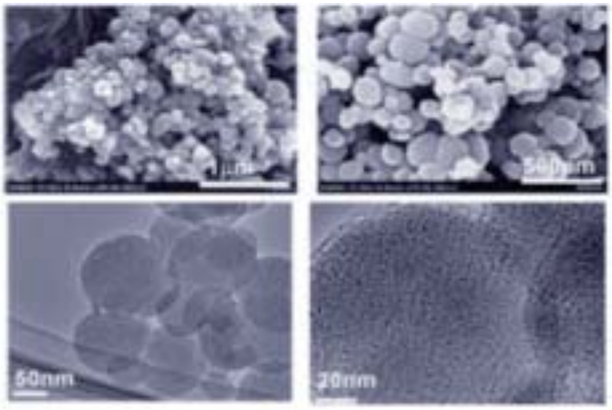

Fig. 1. HR-SEM and TEM images of MCG-1.0 material.

(2) Novel nanoporous materials for drug-delivery and bone tissue engineering systems:

The textural and structural properties of this new family of mesoporous glasses can be controlled by changing the CaO content of mesoporous glasses. A progressive evolution from 2D-hexagonal to 3D-bicontinuous cubic structure with an increase in the textural properties was observed when decreasing the CaO content. The possibility of tailoring both structural and textural features of mesoporous glasses is undoubtedly an attractive advance towards the development of biomaterials that is able to fulfill the essential requirements for specific biomedical applications. In addition, taking into account the ability to introduce different species in the mesoporous matrices that can be subsequently released in a controlled fashion, combining the property with their inherent bioactivity could open new fields of application for these materials (Fig.2).

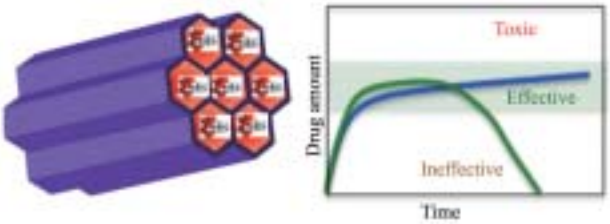

Fig. 2. Incorporation of biomatrices and controlled drug release of nanoporous materials.

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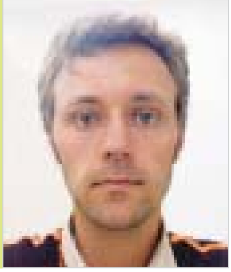
Photovoltaic CIGS Thin Films from Nanoparticle Precursors using Aerosol Deposition

ICYS-MANA Researcher Jesse WILLIAMS



1. Outline of Research

$Cu(In,Ga)Se_2$ is an attractive photovoltaic material because it has a band gap that is optimal for the solar spectrum, and unlike silicon, it has a direct band gap, which means it can efficiently absorb light using only a thin-film of material. Other appealing properties of CIGS are that they are non-toxic and stable. CIGS solar cells have demonstrated conversion efficiencies of about 20% [1)]. These solar cells were produced using vacuum deposition techniques, which offer good control over the deposition conditions. However, vacuum deposition techniques are not scaleable for large area deposition and limited to batch processing, and they are inherently costly.

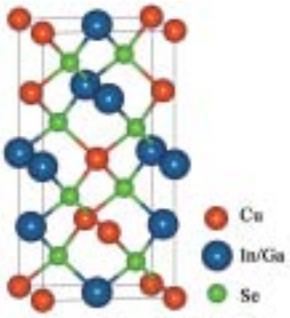


Figure 1. The unit cell of CIGS, which is in chalcopyrite family.

There has been much research investigating non-vacuum deposition techniques such as spray deposition, printing, and depositing from solutions. While these methods are quick, scalable, and cheap, generally, they tend to produce films of inferior material quality compared to their vacuum deposited counterparts. This is because the non-vacuum deposition techniques produce a porous microstructure, and they do not have sufficient control of stoichiometry.

Aerosol deposition is a non-vacuum deposition technique that produced dense films from nanoparticle precursors, and the resulting stoichiometry of the films is dictated by the stoichiometry of the nanoparticles. Thus far, aerosol deposition has been used to form dense films for piezoelectric, capacitors, and ferroelectrics [2,3)]. We aim to produce high-quality fully dense CIGS films from nanoparticle precursors using the aerosol deposition method.

2. Research Activities

(1) Nanoparticle synthesis

CIGS nanoparticles are synthesized using a thermal reflux method. Specifically the process involves heating the reactants in the solvent triethylene glycol to drive the reaction:

$$0.9CuCl + 0.7In + 0.3Ga + 2Se \rightarrow Cu_{0.9}(In_{0.7},Ga_{0.3})Se_2$$

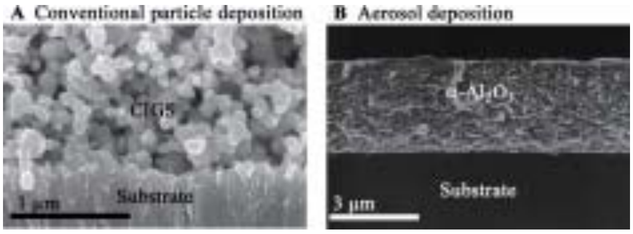


Figure 2. Nanoparticle precursor films deposited by conventional particle deposition (A)[4)] result in high porosity while aerosol deposited films (B)[5)] are fully dense.

It is important to control the stoichiometry of the particles as well as their size because particle size is a key factor for aerosol deposition. The particles must be in the size range 500 nm – 1 µm, and it is possible to tailor particle size by controlling solution concentration, reaction time, and reaction temperature. Nanoparticles of the appropriate phase and size have been synthesized as shown below.

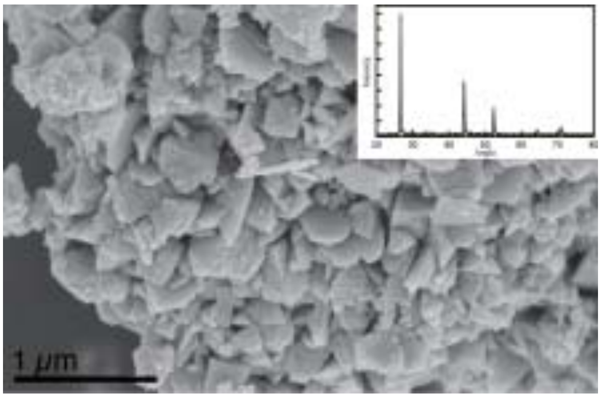


Figure 3. Micrograph showing synthesized CIGS nanoparticles several hundred nanometers in size. Inset: an x-ray diffraction pattern showing a single material phase.

(2) Aerosol deposition

Aerosol deposition uses a pressurized carrier gas to spray the nanoparticle at the substrate surface. The deposition chamber is kept at reduced pressures to maintain high particle velocity. The spray process first abrades the surface clean and then the film begins to deposit. Because the particles are at high velocities, they form a dense film through a process call room temperature impact consolidation.

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Development of Piezoresistive Cantilever Array Sensors

ICYS-MANA Researcher Genki YOSHIKAWA

1. Outline of Research

Microfabricated cantilever arrays (Fig. 1) are emerging as label-free and real-time sensors for detecting tiny amount of various target molecules in parallel. Adsorption of analytes on a receptor layer coated on a cantilever surface induces surface stress, which makes the cantilever bend. This simple mechanics opened a myriad of possibilities for the use of atomic force microscopy (AFM) cantilever deflection technique beyond imaging. Applications ranging from chemistry to genomics have been demonstrated, for example, detection of volatile organic compounds, triggered marker genes, viruses, fungi, etc. In contrast to conventional optical (laser) read-out technique for the measurement of cantilever deflection, piezoresistive read-out system does not require bulky and expensive instrumentation.[1)] This approach contains various advantages, such as low cost, simple operation, miniaturization, and measurements in opaque liquids.

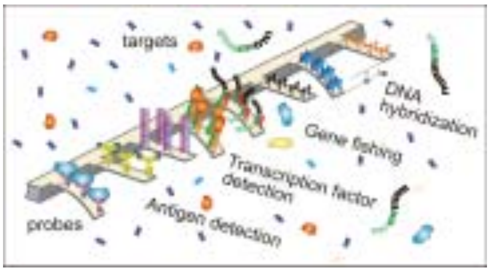

Fig. 1. Bio-functionalized cantilever array sensors.

2. Research Activities

(1) Geometrical optimization for higher sensitivity based on the strain amplification schemes

The scanning applications, such as AFM, are based on the point force applied at the free-end of a cantilever. In this case, strain depends on the position along the cantilever; maximum at the fixed-end and minimum at the free-end. Since the strain depends also on the local geometry of a cantilever, constriction near the fixed-end efficiently enhances the strain. Thus, the piezoresistor embedded on the constriction near the fixed-end will exhibit larger change in resistance compared to that without constriction. In the case of sensing applications, on the other hand, adsorption of analytes on the surface of a cantilever induces uniformly distributed stress, so-called "surface stress". Accordingly, strain is practically independent of a position along the cantilever and piezoresistors can detect only the strain induced just above them in the case of sensing applications.

To optimize the cantilever geometry for sensing applications, algebraic models have been developed and verified by finite element analyses (FEA). With the optimized geometries, the strain can be significantly amplified more than 40 times with the feasible dimensions as shown in Fig. 2.

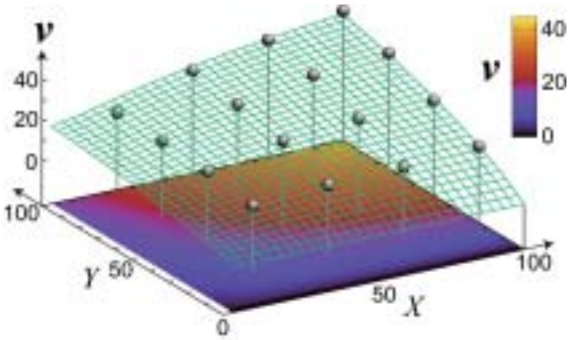

Fig. 2. The optimized strain amplification (ν) for given geometrical factors (*X* and *Y*). Values obtained by the algebraic model are represented as a wire frame and projected onto the *X-Y* plane with color gradation, while the calculated results by FEA are plotted with gray balls.

(2) Analyses of target materials[2)]

Since the piezoresistive cantilever array sensor detects the stress induced on the surface, it could be applicable to monitoring structural changes of thin films, which cause some stress in most cases. Recently, we found that noble metal-intercalated fullerene (C_{60}) can be fabricated by the low temperature co-deposition technique. A silver-intercalated C_{60} is fabricated by depositing Ag and C_{60} simultaneously onto a substrate kept at low temperature (~23 K), suppressing aggregation of cohesive Ag atoms. Detailed analyses of the results of *in situ* conductivity measurements have revealed a granular-metal state of Ag_7C_{60} crystallites dispersed in an insulating C_{60} phase (Fig. 3). While Ag-doped C_{60} will serve as a new platform for hydrogen-storage materials and novel superconductors, it requires further investigation including analyses of the continuous structural changes observed in these measurements. The optimized piezoresistive cantilever array sensors will be useful for *in situ* monitoring of these structural changes, leading to better understanding of this system for various applications.

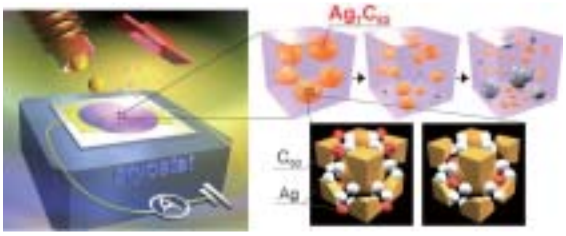

Fig. 3. Schematic illustration of the low temperature co-deposition technique. Ag-intercalated C_{60} (Ag_7C_{60}) exhibits continuous structural change with an increase in temperature.

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Nano-Carbon Materials for Green Energy

ICYS-MANA Researcher Yuanjian ZHANG

1. Outline of Research

Due to the rapid depletion of limited fossil energy sources and the increasingly worsening environmental pollution, the development of alternative energy supply has attracted worldwide attentions. It is expected to be clean, safe, economic and renewable. Development of new energy conversion and storage materials is one first option within direct reach of applications. Among them, electrochemical devices, such as fuel cells, supercapacitors and solar cells are considered to be one of the key components towards step-by-step available solutions.

In terms of fundamental properties and technological innovation, it is well-known that carbon systems are well ahead in the challenge of synthesizing new materials by almost infinite existed molecules in the materials science. And taking advantage of nanotechnology, carbon nanostructures, such as well-known single-walled carbon nanotubes (SWNTs), and fullerenes have attracted great interests in many scientific fields (Figure 1a,b). It has been envied that all these carbon nanostructures are among the excellent candidates as energy conversion and storage media. For example, due to unique excellent conductivity and high specific surface area, SWNTs have showed the significant advance as catalysts supporting materials for fuel cell, and an attractive component for supercapacitors and solar cells. And fullerene bulk heterojuntion solar cells are among the most promising sunlight-to-electric converting devices. However, both SWNTs and fullerene or their derivatives suffered from difficulties, such as high costs, impurities or poor stability.

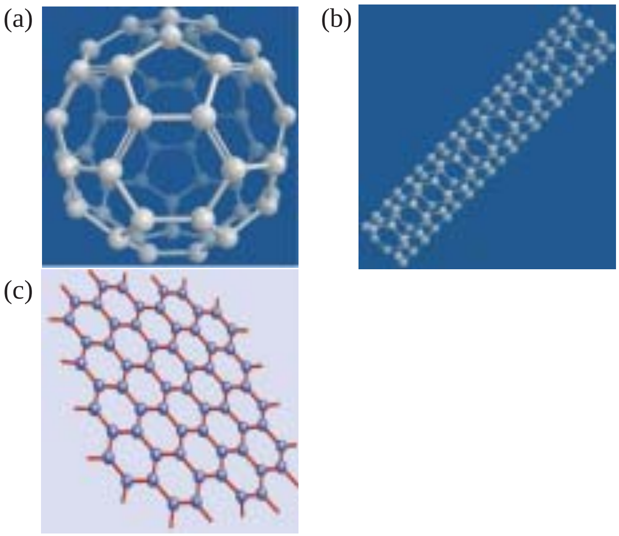

Figure 1. Structures of the different allotropes of nanostructured carbon, (a) zero-dimensional fullerene, (b) one-dimensional nanotubes and (c) two-dimensional graphene.

As another kind of carbon nanostructures, graphene, discovered in 2004, has been a rapidly rising star on the horizon of materials science and condensed-matter physics (Figure 1c). This one-atom thick and two-dimensional layer of sp^2-bonded carbon exhibits exceptionally high crystal and electronic quality, and, despite its short history of rediscovery, has already revealed a cornucopia of new physics and potential applications. Moreover, it is pure, cheap, and environmentally benign. Therefore, graphene is very promising to strengthen present applications of carbon nanostructures.

The present study is focused on the development of graphene-based nanocomposites for the purpose of sustainable electrochemical energy. The chemical functionalization and nano-engineering of graphene aiming tailor the surface decoration, surface area and hierarchical structures for the specific application schemes are involved. Moreover, the correlation between physicochemical properties of modified graphene and its performance in electrochemical energy devices will be emphasized. The work will be beneficial not only to the active and growing fundamental physicochemical studies of graphene, but also to the future applications of graphene in energy fields.

2. Research Activities

(1) Isolation of graphene sheets and its functionalization

Because dispersion of graphene without aggregate is a vital process in its applications, the first step is to isolate and disperse graphene sheets by investigating its chemistry. Fortunately, examples have been given in chemistry of graphite, fullerenes and SWNTs, and some possible reactions of graphene have also been predicted, but due to its unique 2D structure, graphene would illustrate different reaction activities. For example, covalent and non-covalent reactions as well as new reactions are conducting.

(2) Physicochemical properties

Studies are beginning to investigate their optical, electronic and crystalline properties as well as morphologies by Raman, UV-vis spectrascopy, FT-IR, XRD, BET, AFM, SEM, and TEM. Moreover, the applications of derived graphene in fuel cells, supercapacitors and solar cells are under investigation

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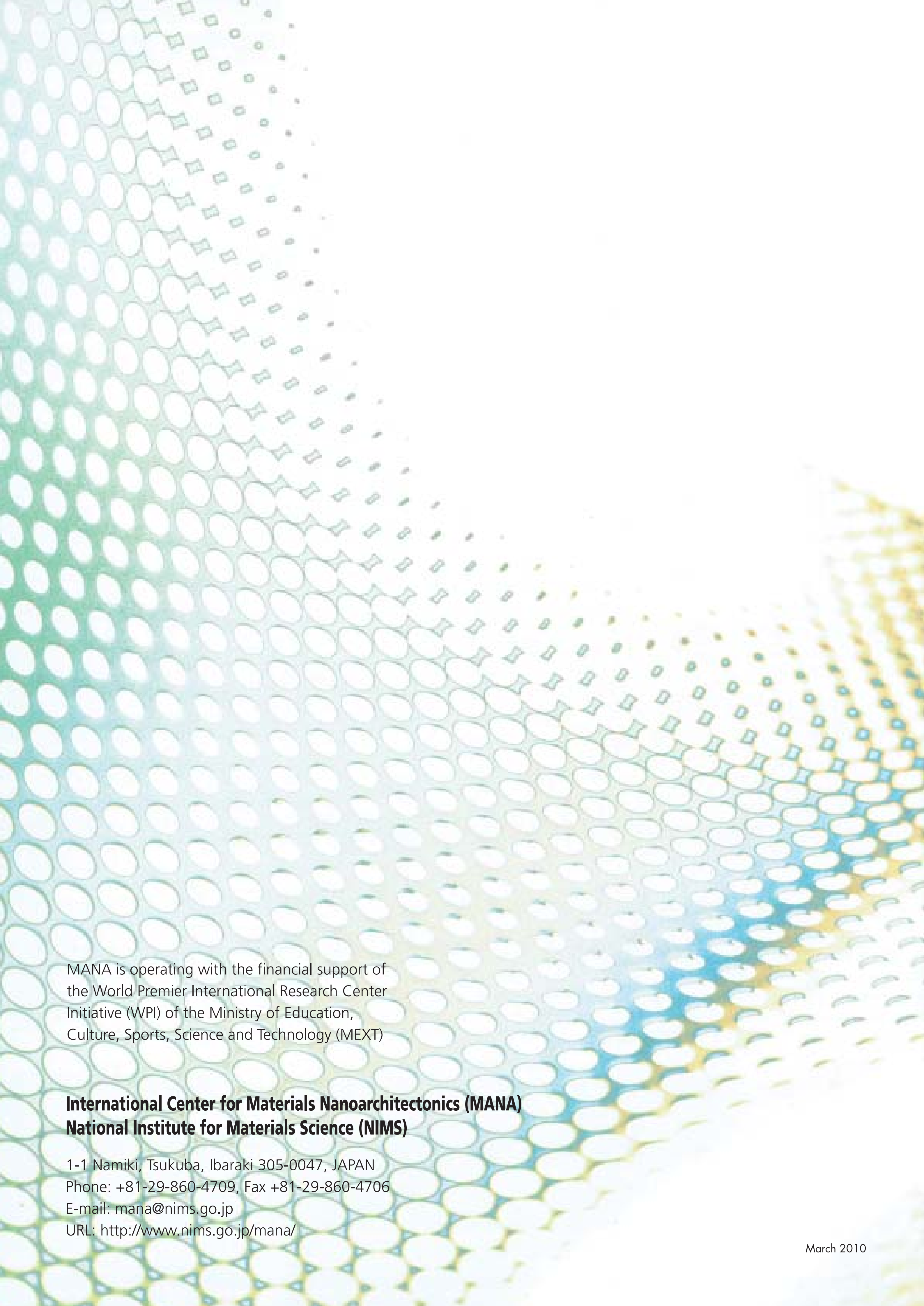

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