MANA Progress Report

Research Digest 2012

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

National Institute for Materials Science (NIMS)

Preface

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MANA Director-General
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MANA was founded in October 2007 with the support of the World Premier International Research Center Initiative (WPI Program) of Japan's Ministry of Education, Culture, Sports, Science and Technology (MEXT). The WPI program aims "to build globally visible research centers that boast a very high research standard and outstanding research environment, sufficiently attractive to prompt frontline researchers from around the world to want to work in them." MANA has made considerable progress toward achieving this aim during the first five-year period of the WPI Program (2007-2011). This is made clear by the high praise MANA received in the WPI Program Committee's interim evaluation in 2011.

However, we, the scientists of MANA, are not satisfied with this accomplishment. We want to tackle even more challenging research during the next five years. The future challenges of MANA were discussed at MANA's 5th Anniversary Memorial Symposium held in the new WPI-MANA Building in October 2012.

This booklet, which is the part "Research Digest 2012" of the MANA Progress Report, summarizes the research activities of *MANA Principal Investigators*, *Group Leaders, MANA Associate Principal Investigator*, *MANA Independent Scientists* and *ICYS-MANA Researchers* in the calendar year 2012. *MANA Principal Investigators* are internationally known world-top class scientists, who take the main role to achieve the MANA research targets and serve as mentors for younger researchers. MANA has selected Principal Investigators from NIMS and other domestic and overseas institutes. A *Group Leader* heads a research group of a research unit led by one of the Principal Investigators. An *Associate Principal Investigator* is a promising young scientist, who is expected to perform his own research as almost comparable to a Principal Investigator. *Independent Scientists* are younger researchers at NIMS, who work full-time for MANA and can perform their own research independently. *ICYS-MANA Researcher* is a position for postdoctoral fellows selected from all over the world by open recruitment. ICYS-MANA Researchers perform their own research independently by receiving advice from Mentors and MANA Principal Investigators. Other information on MANA research achievements (e.g., the lists of publications and patents) is given in the part "Facts and Achievements 2012" 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 2012

MANA Principal Investigators (23)

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Nano-System Field

Nano-Power Field

Nano-Life Field

Group Leaders (11)

MANA Associate Principal Investigator (1)

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Inorganic Nanosheets

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1. Outline of Research

We aim at synthesizing two-dimensional (2D) inorganic nanosheets as a unique class of nanoscale materials by delaminating various layered compounds through soft-chemical processes. Particular attention is paid to fine control of their composition and structure via doping and substitution of constituent elements, expecting new or enhanced properties.

We develop a new nanofabrication process for precisely organizing functional nanosheets into multilayer or superlattice assemblies through solution-based processes (Fig. 1). Based on this novel approach with the nanosheets (soft-chemical materials nanoarchitectonics), we establish the tailoring ability and controllability over nanostructures with a precision down to 1 nm, which is comparable to that in lattice engineering utilizing modern vapor-phase deposition techniques.

In the second stage, we take challenges to develop innovative nanostructured materials and nanodevices through nanoscale assembly of nanosheets and a range of foreign modules (organic compounds, metal complexes, clusters...). Particularly we attempt to realize new or sophisticated functions by cooperative interaction between nanosheets themselves or between nanosheets and other functional modules.

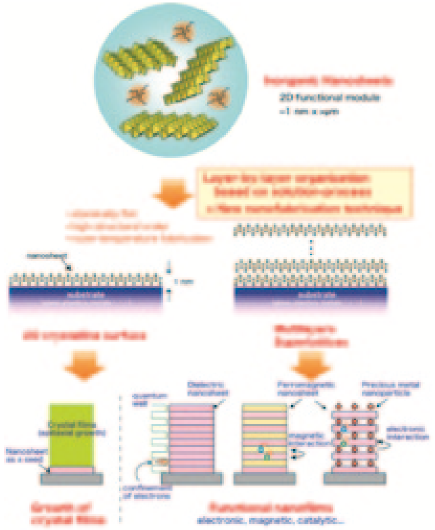

Fig. 1. Conceptual explanation of the research plan.

2. Research Activities

(1) Synthesis of Niobate Nanosheets with a Finely Controllable Thickness.[1)]

Niobate nanosheets of $Ca_2Na_{n-3}Nb_nO_{3n+1}^-$ ($n \geq 3$) were synthesized by delaminating a homologous family of layered perovskite compounds through soft-chemical reaction with quaternary ammonium ion. Total delamination was confirmed by *in situ* XRD analysis. AFM observations detected micrometer-sized 2D crystallites having a progressively increasing thickness by 0.4-0.5 nm with *n* (Fig. 2), which corresponds to the height of NbO_6 octahedron. This series of nanosheets provides an ideal stage to gain insight into a structure-property relationship for ultimate 2D oxide systems. The bandgap estimated from their optical absorption edge was 3.96, 3.81, and 3.77 eV for n = 4, 5, 6, respectively, which may reflect the relaxing degree of size quantization with the nanometer-scale thickness. These nanosheets are promising as a functional building block for electronic and photochemical applications.

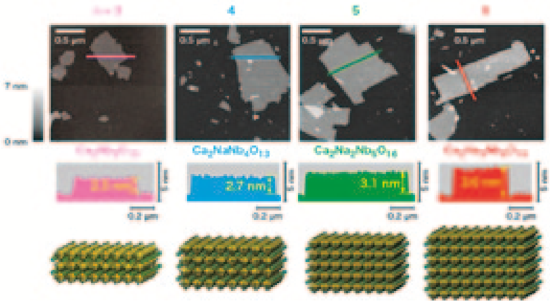

Fig. 2. AFM images of niobate nanosheets, $Ca_2Na_{n-3}Nb_nO_{3n+1}^-$.

(2) Synthesis of Layered Transition Metal Hydroxides.[2-3)]

Topotactic oxidation of various transition-metal brucite hydroxides, recently developed by us as a new protocol to synthesize layered double hydroxides (LDHs) (Fig. 3), was studied in depth. We found that transformation into LDH structure strongly depends on the metallic composition (Fe, Co, Ni) of brucite samples and oxidizing agents (I_2 and Br_2). The comprehensive understanding obtained on the process enables the fine-control over the composition, charge density, staging structure and so forth, which will lead to a new class of all-transition-metal LDH nanosheets.

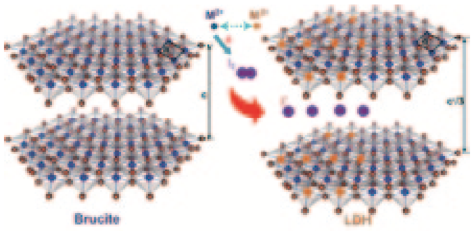

Fig. 3. Schematic illustration for transformation from brucite hydroxide to LDH.

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Supramolecular Materials

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1. Outline of Research

Functional materials have been wisely constructed via bottom-up approaches as seen in preparation of molecular and nano patterns, complexes, and nanomaterials organized nano- and microstructures, and function materials. In addition, novel concepts to bridge nano (molecular) structures and bulk systems now becomes crucial in order to control real nano and molecular functions from our visible worlds. We have proposed a novel methodology "hand-operating nanotechnology"[1-2] where molecular orientation, organization and even functions in nanometer-scale can be operated by our bulk (hand) operation. Selected examples of research results on supramolecular materials are shown below.

2. Research Activities

(1) Mechanically-Controlled Indicator Displacement Assay.[3]

Mechanical compression was applied to a host monolayer at an interface, which facilitated an indicator displacement assay (Fig. 1). The fluorescence resonance energy transfer (FRET) between the host and indicator was "switched on" by this compression. Addition of D-glucose caused the indicator to be displaced, effectively quenching the FRET process. Thus, the novel concept of a mechanically-controlled indicator displacement assay (MC-IDA) was successfully achieved.

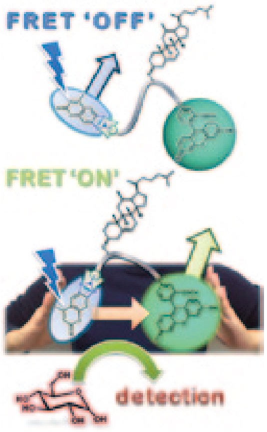

Fig. 1. Mechanically-Controlled Indicator Displacement Assay.

(2) Flake-Shell Capsules: Adjustable Inorganic Structures.[4]

Structure-adjustable capsules have been fabricated from inorganic components by using a self-template dissolution-regrowth mechanism, giving flake-shell silica microcapsules (Fig. 2). The capsules shrink under thermal stimulus and their structures can be adjusted by treatment at different pH. Tuning of shell pore diameters leads to tailored drug release over prolonged periods.

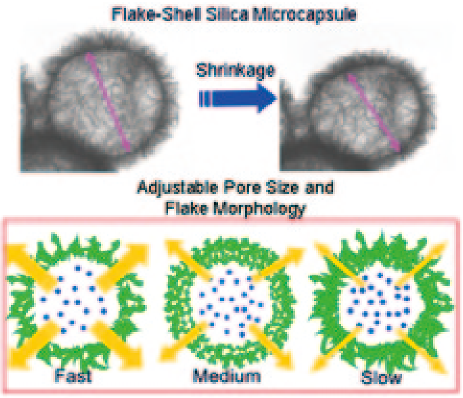

Fig. 2. Flake-Shell Capsule and Controlled Drug Delivery.

(3) Silica-based Gene Reverse Transfection.[5]

Substrate-mediated reverse gene transfection was developed from a silica film composed of an upright-sheet network (Fig. 3). The silica film was prepared by a simple one-pot process from a flat silica layer on a silicon substrate. The dense upright-sheet network exhibits high surface activity and surface area, which favor the immobilization of DNA and subsequent cell transfection even in the absence of matrix proteins. Transgene expression efficiency of the silica film was approximately double that observed for solution-based transfection.

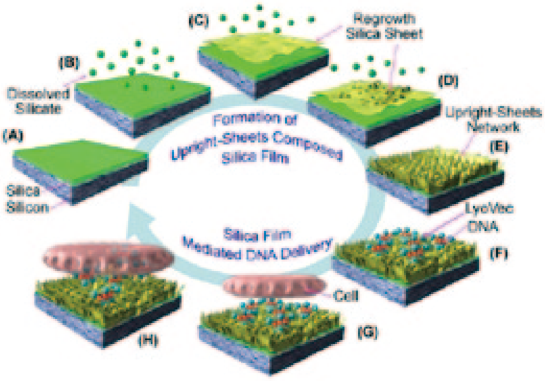

Fig. 3. Silica-Based Gene Reverse Transfection.

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Inorganic Nanostructured Materials

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1. Outline of Research

Our ultimate goal is to explore novel inorganic nanostructured materials such as nanotubes, nanowires and nanoparticles and their applications in energy storage and composite material fabrication etc.

In order to accomplish this purpose, we set up a full set of instruments for synthesis and characterization of nanomaterials, including induction furnace, electrochemical station and transmission electron microscope etc, which enable us to effectively control synthesis of various nanomaterials, investigate their energy storage capability and adopt them as fillers for polymer composites with excellent performances.

2. Research Activities

(1) ZnO Hollow Spheres Structure for High-Performance Photodetectors.[1)]

Inspired by opening soft drink cans, we developed a one-pot method to prepare ZnO hollow spheres with double-yolk egg architectures (DEHs, Fig. 1). The bubble-assisted Ostwald ripening is suggested to be responsible for the formation of these novel structures. The uniqueness of DEHs morphology leads to enhanced photodetector performance.

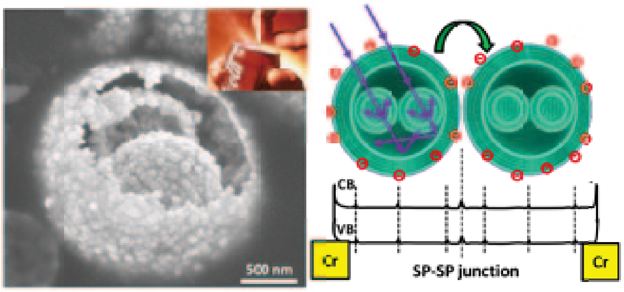

Fig. 1. (left) SEM image of ZnO hollow spheres with double-yolk egg structure; (right) Schematic illustration of multi-reflections within the DEHs structures and the SP-SP junction barriers under the electron transfer within the present unique architecture, showing an increase of the light-harvesting efficiency and lowering of the SP-SP junction barrier height from the light-off to light-on states.

(2) High-Performance Lithium-Ion Batteries by N-Doped Graphene-SnO_2 Sandwich Paper.[2)]

A new facile route to fabricate N-doped graphene-SnO_2 sandwich papers is developed. The 7,7,8,8-tetracyanoquinodimethane anion (TCNQ) plays a key role for the formation of such structures as it acts as both the nitrogen source and complexing agent. If used in lithium-ion batteries (LIBs), the material exhibits superior electrochemical performance (Fig. 2). It results from its unique features: excellent electronic conductivity due to the sandwich structure, short transportation length for both lithium ions and electrons, and elastomeric space to accommodate volume changes upon Li insertion/extraction.

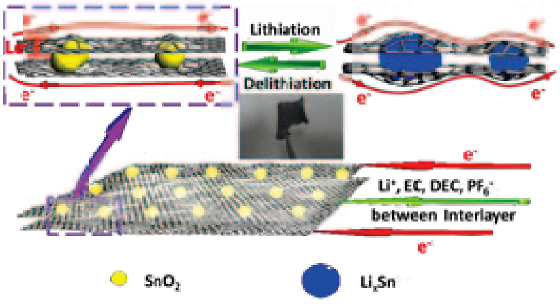

Fig. 2. Schematic representation showing paths for lithium-ions and electrons (L_e) in the N-doped G-SnO_2 paper, respectively. Inset showing the real product appearance.

(3) Boron Nitride Nanotube Nanocomposites with High Thermal Conductivity.[3)]

We successfully fabricated an ideal dielectric thermally conductive epoxy nanocomposite by functionalized boron nitride nanotubes (BNNTs) as fillers (Fig. 3). The nanocomposites with 30 wt% fraction of modified BNNTs exhibit much lower dielectric constant, and coefficient of thermal expansion in comparison with the pure epoxy resin. The nanocomposites show a thermal conductivity enhancement of 1360% in comparison with the epoxy resin at the BNNT loading fraction of 30 wt%.

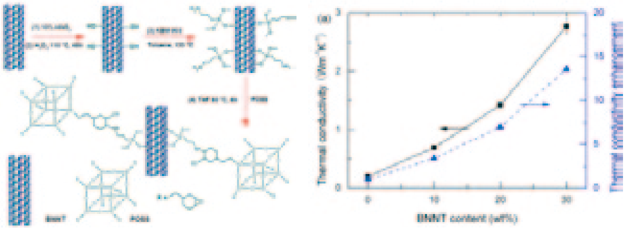

Fig. 3. (left) Schematic diagram illustrating fabrication of functionalized BNNTs; (right) Thermal conductivity improvement of BNNT/epoxy composites.

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Nano Electrics and Related Materials

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1. Outline of Research

In the future large scale integrated circuit (LSI), due to the scaling of the transistors, new materials exploration and atomically controlled nano interfaces are required.[1] Presently a stack of HfO_2 and SiO_2 are used in a micro processor and this materials will be adopted in memory devices too. However to realize more smaller transistor, another new gate oxide materials, which can contact with Si directly, will become the most serious issue, though a lot of efforts have been made to find new candidates of having higher dielectric property to find the next generation "high-k" materials. For this purpose, La_2O_3 or CeO_2 has been extensively studied.[2] To find confirmable metal gate, work function tuning, structure control and thermal stabilities are the key factors in materials screening. To control the work functions, two kinds of metals, which have higher work function and lower work function, are mixed to compose nano-CMOS device. As well recognized, though the work function was successfully tuned, it did not reflect the threshold voltage (V_{th}), due to the Fermi level pinning.[3] The other emerging issue is the fluctuation in device performance, such as V_{th} fluctuation in nano CMOS. It is not clearly identified how the V_{th} fluctuates, but some candidates for explanations are pointed out. One of them is edge roughness which comes from polycrystalline structure of the metal gate composed of grains in 20nm – 200nm, which are larger than that of gate length. For realizing ideal metal gate, the material must be amorphous with work function tenability and thermal stability with high-k insulator. In this work, we refer to the new materials exploration at first and showed a successful result of new finding in metal gate materials.

2. Research Activities

(1) Combinatorial materials synthesis.

As the new materials exploration tool, the combinatorial synthesis becomes prevalent in the last a decade for the materials research. Recently, we demonstrated the combinatorial ternary alloying as an innovative tool for thin film synthesis[4] to cover the whole composition. The concept of this combinatorial synthesis is illustrated in Fig. 1a. In this method, the sample rotation and moving mask system was synchronized to form a thin composition spread film. The advantage of this method is the continuous composition spread accompanied by three kinds binary alloying regions as shown in Fig. 1b. This method was already applied for new gate oxide of HfO_2-Y_2O_3-Al_2O_3 films.[5] This method can be applied to the ternary metal alloying to screen the metal gate materials as demonstrated in Fig. 1b.

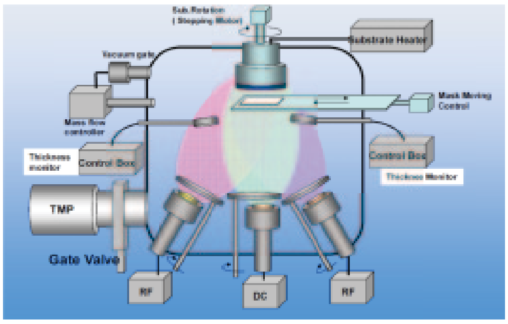

Fig. 1. Schematic illustration of a combinatorial samples of metal alloys by sputtering.

(2) New amorphous metal gate of Ta-Y-C.[6]

A candidate of amorphous structured metal gate is Ta – Al because the Ta and Al has more than 15% atomic size difference and has a great possibility of having amorphous structure by alloying. Also the Ta-Al has another possibility of work function tuning. Doped C as the impurity will extend the possibility of thermally stable metal alloy on high-k oxide. Fig. 2 shows a result of flat band shift of Ta-Al-C alloy and sample structure for measurement. Surprisingly a large flat band shit was observed. An in-depth profiling showed the Al diffusion from Ta-Al alloy to form a Al_2O_3/SiO_2 stacked structure.[7] It was well known that there is a dipole formation at Al_2O_3/SiO_2 and it was thought this dipole contributed to the large flat band shift. The shift value was 0.4 eV, which can contribute to CMOS operation. These results showed that Ta-Al-C alloying had a great possibility as the metal gate materials for the future nano CMOS devices.

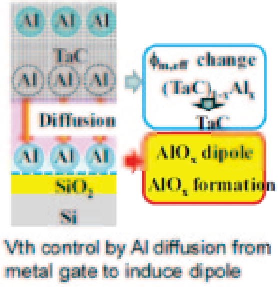

Fig. 2. Flat band shift due to work function tuning by Ta-Al-C alloying. The shift was 0.4eV.

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Nanomaterial Mechanics Analyzed in TEM

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1. Outline of Research

Nanomaterials, like nanotubes, nanowires and nanosheets, are envisaged to greatly contribute to the Structural Materials Field of the 21st century. In theory, they are strong, elastic and tough, while breaking many world-records in regards of ultimate tensile strength and Young's modulus. However, in practice, those *nano*-properties could rarely been experimentally accessed due to a tiny object lateral size and non-availability of practical experimental setups for analyzing mechanical performance at the ultimately downsized scales. The modern microscopic technique utilized by the Nanotubes Group, *i.e.* atomic force microscope (AFM) unit merged with a high-resolution transmission electron microscope (HRTEM), allows one to precisely *in situ* measure the strength, plasticity and elasticity of any individual nanostructure, and even to find its smart utilization for reinforcing practically important lightweight metals, for instance, common Aluminum.

2. Research Activities

(1) *Mechanical behavior of ultrathin Silicon nanowires.*

Deformation and fracture mechanisms of ultrathin Si nanowires (NWs), with diameters down to only ~9 nm, under uniaxial tension and bending in TEM were for the first time analyzed, Fig. 1.[1)] The mechanical behaviors were closely related to the wire diameter, loading conditions and stress fields. Under tension, Si NWs deformed elastically until abrupt brittle fracture. The tensile strength showed clear size dependence, and the highest strength values of ~10-11 GPa were documented for thinner wires; these numbers are close to the ideal theoretical strength of Silicon. In contrast, under bending, the NWs demonstrated a considerable plasticity. Under a bending strain of <14 % they could repeatedly be deformed without cracking along with a crystalline-to-amorphous phase transition. Under a larger strain of >20 % the cracks nucleated on the tensed side and propagated from the wire surface, whereas on the compressed side a plastic deformation took place due to dislocation activities and an amorphous transition.

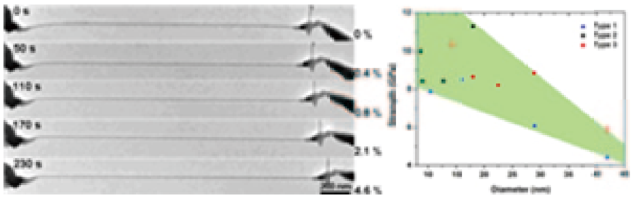

Fig. 1. **(left) An individual Silicon nanowire tensile-tested in TEM, the running time is marked on the consecutive video-frames; (right) a plot of the tensile strength dependence on a nanowire diameter; generally, the strength increases with decreasing a NW diameter. Variously shaped and colored experimental data points correspond to different types of wire failures.**

(2) *Tensile properties of novel Al-BNNT nanocomposites.*

Boron nitride nanotubes (BNNTs) are structural analogs of carbon NTs, but exhibit much higher chemical, thermal and oxidation stabilities; such parameters are of prime importance for practical utilizations in prospective metal matrix nanocomposites. Taking an advantage of huge tensile strength of an individual multi-walled BNNT (>30 GPa) we prepared new sandwich-like nanocomposites consisting of a single BNNT core, ~50 nm in diameter, and a lightweight Al shield, ~20-300 nm thick, using magnetron sputtering. Then, we performed direct tensile tests on such nanocomposites in TEM (Fig. 2).[2)]

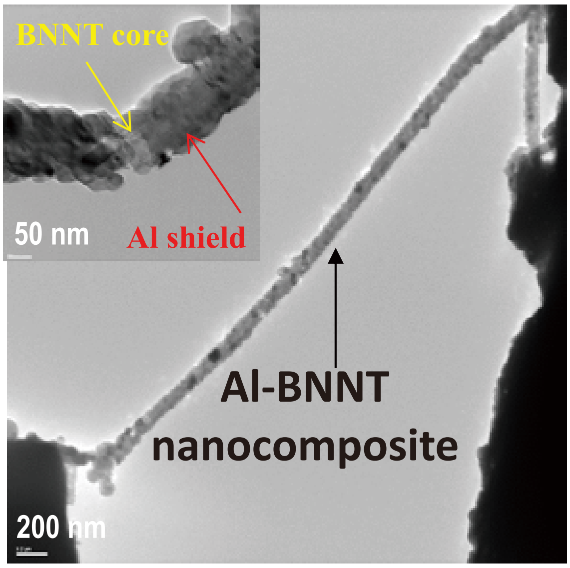

Fig. 2. **An individual Al-BNNT nanocomposite, made of a multi-walled BNNT core and a microcrystalline Al shield, tensile-tested at room temperature inside TEM. The newly constructed hybrid revealed tensile strength of > 360 MPa, thus prevailing that of a standard Al metal for more than one order of magnitude.**

Depending on the Al-shield thickness, the newly created hybrids demonstrated an ultimate tensile strength in the range of 360-1400 MPa,[2)] thus revealing a dramatic, more than a 10-fold increase of this parameter compared to a pure, non-armed Al metal. These pioneering results open up a bright potential for making ultralight and superstrong "dream" structural Al-based materials for future automotive, aerospace and/or other structural applications.

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Superconducting Quantum Nanoarchitectonics

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1. Outline of Research

Our research objective is to develop a new research field in materials science, which is referred to as Nanoarchitechtonics, especially in superconductivity using highly developed modern nanotechnology in the ultimate quantum regime of materials. The challenge to accomplish this concept has been set forth on the intrinsic Josephson junctions (IJJ's) with and without magnetic field 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 novel phenomenon was discovered in the mesa structure of this material: strong, continuous and coherent electromagnetic waves at THz frequencies were observed. From the sharp spectrum of the radiation (~0.5 GHz) it is considered as LASER emission from stacked intrinsic Josephson junctions in the mesa. This achievement has triggered much interest because the device may bring us the first full solid state THz sources, which will enable us a variety of important applications in the 21st century.

Here, we had a progress one step further and resolved an important issue concerning THz radiation: the Joule heating effect during emission of THz radiation because of the dc current dissipation in the mesa.

Concerning new materials, we have started to grow high quality topological insulating materials such as Bi_2Se_3, Bi_2Te_3, $Pb_{1-x}Sn_xTe$, *etc*. and studied their fundamental properties such as Hall effect, de Haas van Alphen effect (dHvA) up to 60 T, and superconductivity, *etc*.

2. Research Activities

(1) Hot-Spot Issues.

It has been pointed out that the temperature of the mesa is significantly raised during THz radiation due to the Joule heating. In fact the heat generated can be estimated easily and turns out that it amounts to ~MW/cm^3, which is gigantic that the temperature of the mesa may be well-above the bath temperature T_{bath}. Furthermore, the local heating phenomenon known as the hot-spot has been claimed by the LTSLM (Low Temperature Scanning Laser Microscopy) technique.[1-2] However, this technique does not measure the temperature of the sample directly, so that the experimental result has not been entirely conclusive.

We developed a new method to measure directly the local temperature by using photoluminescence of SiC, whose micro crystalline powder was directly painted on the surface of the mesa, since the photo luminescence intensity of the SiC has a steep temperature coefficient below about 100 K as shown in Fig. 1(a). We used blue light, which seems to be most sensitive in all temperature regions. Fig. 1(b) and 1(c) show the direct microscope images of luminescent intensities from the mesa with I=0 mA and I=40.1 mA at T_{bath}=15 K, respectively. The image in Fig. 1(c) is analyzed and the temperature obtained is plotted by color codes in Fig. 1(d). As seen here a clear hot spot formation is found. It is surprising that the temperature at the central part of the hot spot is much higher than T_c=80 K. The temperature profile along the white line in Fig. 1(d) is shown.[3)]

Although the hot spot formation is clearly observed, especially at higher current region above I=20 mA, we observed strong THz radiation. Similarly, the THz radiation with almost same frequency is also observed in a very low current region. It turns out by more elaborated study that the hot spot formation is not relevant to the THz radiation at all. This remarkable result posed a serious question to the previous interpretation of the results,[1-2)] which strongly suggested the important role of the hot spot for the THz radiation mechanism.

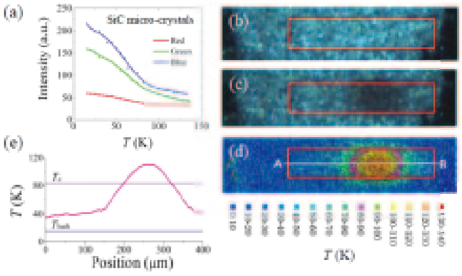

Fig. 1. (a) The temperature dependences of the photoluminescence intensity of SiC for three different colors. (b) and (c) The optical microscope images of the mesa shown by the red square for *I*=0 and 40.1 mA. (d) the temperature map analyzed by using data shown (a) is shown by color codes. (e) The temperature profile along the line A shown in (d).

(2) Transport Study of Topological Insulating Materials.

We have succeeded in growing high quality single crystals of topological insulators Bi_2Se_3:Cu, $Bi_{1.5}Sb_{0.5}Te_{1.8}Se_{1.2}$ $Pb_{1-x}Sn_xTe$ etc. and have performed the ARPES[4)] and transport measurements such as resistivity, Hall effect, de Haas van Alphen effect *etc*. In particular, ARPES in $Cu_xBi_2Se_3$ shows a clear Dirac cone behavior even in the superconducting state with x=0.1-0.2. This strongly suggests that this compound exhibit the Majorana state. Using this sample we started to measure the magneto transport oscillations and Hall effects to characterize Majorana fermion state. The preliminary results show a giant dHvA oscillation at high fields above 40 T, which strongly resembles the magneto-oscillation in graphene and approaches to the quantum limit at higher fields.

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Hybrid Cell for Harvesting Multi-Type Energies

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1. Outline of Research

Although it is rather challenging to solve the large-scale world energy need, energy harvesting is a technology by which ambient energy is extracted from the environment and converted into electricity to power electronic devices.

Researchers have developed several approaches for harvesting solar, thermal, mechanical, and chemical energies, but all of the approaches are targeted at one type of energy for one type of particular applications, while the rest of the other types of energies are wasted. To fully utilize the energy in the environment, a hybrid cell (HC) has been developed for conjunctional harvesting of multiple types of energies using an integrated structure/material so that the energy resources can be effectively and complimentarily utilized whenever and wherever one or all of them are available.

Semiconductor one-dimensional nanostructures, a subset of these materials, have received significant attention for their unique properties and complex structures especially in energy harvesting technology. Many nanostructure-based materials are promising candidates for multi-type energy harvesting devices. The birth of HC devices could be important for developing innovative technologies towards maintenance-free, self-powered systems without batteries or at least extend the lifetime of batteries. This is particularly attractive for wireless sensor networks, environmental monitoring, biomedical devices, and personal electronics.

2. Research Activities

We demonstrate a flexible fiber based HC consisting of a fiber nanogenerator (FNG) and a fiber biofuel cell (FBFC), which can be used in bio-liquid (such as blood) for energy harvesting. The design of the FNG is based on the textured ZnO NW film grown on the surface of the carbon fiber. The carbon fiber serves not only as the substrate on which the ZnONW film is grown, but also as an electrode (noted as core electrode). In previous work we have fabricated a textured ZnO NW film by using physical vapor deposition. The FNG was fabricated by etching the ZnO NW film at one end of the carbon fiber, contacting the top surface using silver paste and tape, and leading out two electrodes from the surface and the core electrodes (left-hand in Fig. 1a). An FBFC, which is used for converting chemical energy from bio-fluid such as glucose/blood into electricity, is fabricated at the other end of the carbon fiber (Fig. 1a). A layer of soft epoxy polymer is coated on the carbon fiber as an insulator, then two gold electrodes are patterned onto it and coated with carbon nanotubes (CNTs), followed by immobilization of glucose oxidase (GOx) and laccase to form the anode and cathode, respectively. In comparison to conventional biofuel cells and miniature biofuel cells, the FBFCs described here were integrated with the NG on an individual carbon fiber, forming a self-powered nanosystem.

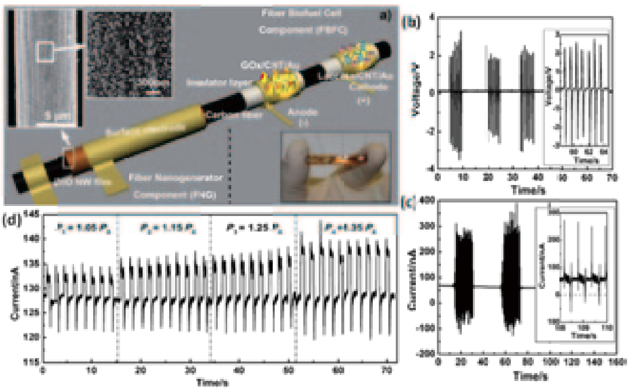

Fig. 1. Characteristics of Hybrid Cell. (a) Schematic 3D representation of the hybrid nanogenerator. The inserts in the upper left are SEM images of a textured ZnO NW film grown around a carbon fiber. A digital image of the device is shown at the lower corner. (b) Open-circuit voltage of the hybrid NG when the FNG and the FBFC are connected in series. (c) Short-circuit current of the hybrid NG when the FNG and the FBFC are connected in parallel. (d) Response of the hybrid NG system to periodically applied pressure.

The performance of the HC is characterized by measuring the short-circuit current Isc and the open-circuit voltage Voc. By integrating the AC FNG and DC FBFC, a HC is obtained with the output close to the sum of the FBFC and the FNG (Fig. 1b and c). The shape and frequency of the AC FNG output are the same before and after the hybridization process, only the base line shifts from zero to the FBFC output. The peak value of the HC open-circuit voltage is ±3.1 V when they are in series; the peak value of the shortcircuit current is 300 nA and -100 nA, when they are in parallel. Theoretical calculations have shown that, within the elastic linear mechanics regime, the output voltage of a single nanowire is proportional to the magnitude of its deformation. An increase on the pressure applied to the ZnO NW film leads to an increase of piezopotential, resulting in a higher current jump in the circuit. Current as a function of applied pressure is shown in Fig. 1d. As the applied pressure increases from ambient atmosphere P_0 to $1.05P_0$, $1.15P_0$, $1.25P_0$, and then $1.35P_0$, the response current increases from 128 nA to 135 nA, that is, by roughly 7%. The sensitivity for the pressure measurement demonstrated here is 1.35%.

This demonstration means that we can monitor the pressure in aliquid, such as blood pressure in blood vessel, by monitoring the current change in the circuit. Such system can be used not only for monitoring blood pressure, but also for monitoring the operation of gas/water/oil pipes. Our hybrid nanogererator is likely to have applications in implantable biomedical devices and environmental/ infrastructure monitoring.

Nano-System Architectonics

MANA Principal Investigator **Masakazu AONO**
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MANA Research Associate Kewei Liu, Rui Yang, Marina Makarova

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 of “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 communi- cation and environmental and energy sustainability. To achieve this interdisciplinary research, we make close collaboration with other research groups in MANA (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), and Prof. Christian Joachim (CEMES-CNRS, France).

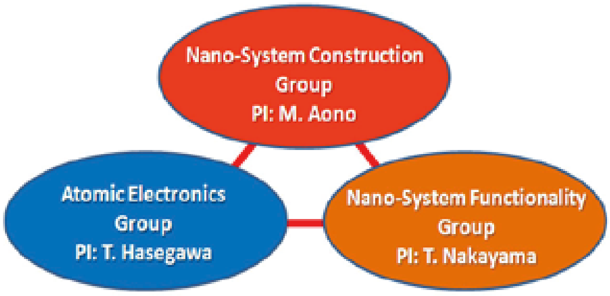

Fig. 1. Collabotration of the Nano-System Construction Group with other groups in MANA.

2. Research Activities

Our research activities are classified into four subjects:

1) Novel nanochemical control: For example, controlled chain polymerization for the formation of electrically conductive polymer chains at designated positions and its application to wire single functional molecules with firm “chemical soldering” aiming at the realization of single- molecule electronics.
2) Atomic switch and related devices: a) Practical application of the atomic switch to field programmable gate arrays. b) Utilization of the synaptic properties of the atomic switch to develop novel neuromorphic computational circuits.
3) Novel scanning-probe microscopes (SPMs): a) Novel SPMs for nanoscale magnetic imaging without using a magnetic probe. b) Multiple-probe SPMs for local nanoscale electrical conductivity measurements.
4) Theoretical studies of strongly-correlated electron system: For example, the essential understanding of Mott transition.

In the following, subject 4) will be discussed in more detail. The metal-insulator transition due to Coulomb repulsion is called the Mott transition. We theoretically show that the Mott transition is characterized by freezing of the charge degrees of freedom in a single-particle excitation that leads continuously to the magnetic excitation of the Mott insulator. By revealing the nature of the Mott transition, various anomalous features observed in cuprate high-temperature superconductors are explained in a unified manner as properties of a two-dimensional model near the Mott transition (Fig. 2).

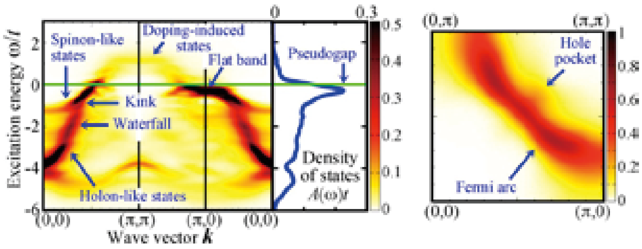

Fig. 2. Spectral intensity of single-electron excitations $A(k, \omega)$ near the Mott transition in a two-dimensional model. The figure at the right shows $A(k, \omega \approx 0)$.

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MANA Brain: Neuromorphic Atomic Switch Networks

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MANA Scientific Advisor Adam Z. Stieg
Postdoctoral Scholars Greg Pawin, Cristina Martin-Olmos, Hsien-Hang Shieh
Graduate Student Researchers Audrius Avizienis, Henry Sillin

1. Outline of Research

Our research is focused at integrating experiment and theory to create a functional atom-switch neuromorphic device that implements basic concepts of systems neuroscience. The realization of such a system involves the development of a complex network of interacting non-linear elements capable of generating emergent behaviors considered fundamental to brain function. By combining self-assembly of nanoscale architectures, electrochemistry and solid-state electroionics, atomic switch networks (ASN) represent a unique class of physical devices capable of exhibiting synapse-like properties in neurally-inspired architectures. The unique properties provided by ASNs represent a clear departure from CMOS-based computation, exhibit striking similarity to biological systems, and represent a radically alternative pathway for the creation of intelligent machines.

2. Research Activities

Atomic switch networks (ASN) have been shown to generate network level dynamics that resemble those observed in biological brains.[1,7] In 2012, we extended upon our prior experimental work in two directions:

(A) Modeling and Simulation- To facilitate understanding and control of the dynamical ASN, we developed a numerical model based on the physical properties of individual atomic switches and the interconnected nature of the ASN, which has been validated against various experimental results including: network activation, distributed conductance, controlled plasticity via feedforward subassemblies, and harmonic generation (Fig. 1).

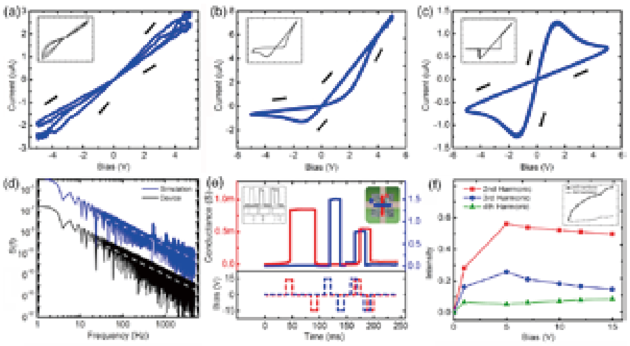

Fig. 1. Validation of numerical model (main) with experiment (insets). (a-c) Device activation (d) log-log power spectral density (e) 2-bit feed-forward switching and (f) higher harmonic generation.

(B) Reservoir Computing – Most attempts to mimic the brain's function employ simulated neural networks where recurrently connected nodes allow information to be integrated at different time points, enabling online training. The drawbacks of recurrent networks reside in the difficulty of adjusting connective weights within the network and the vast computational degrees of freedom to permit convergence in a reasonable time. Reservoir Computing (RC) has been developed to overcome these issues, while retaining biologically relevant features. RC methods enable the performance complicated classification tasks using simple linear regression techniques alongside generalization of learned tasks in real time (Fig. 2).

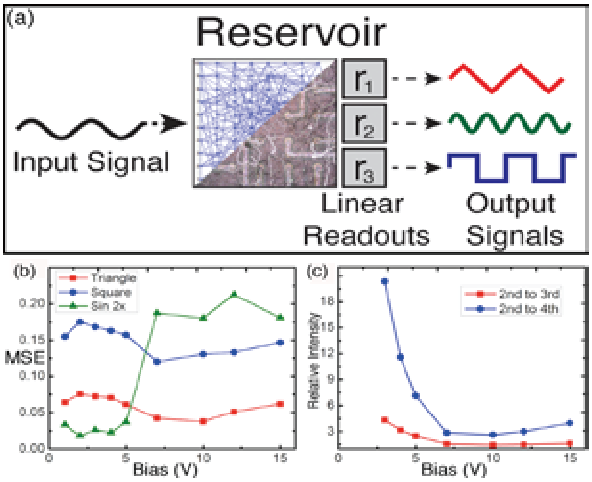

Fig. 2. a) Schematic of network simulation used in a waveform generation RC task, implemented using a 10x10 network to produce triangle, square and sinusoidal waveforms. b) Mean-squared error (MSE) for each task with respect to driving amplitude Performance in the sinusoidal waveform task decreased when c) the relative amplitude of the 2nd harmonic becomes increasingly diminutive.

We recently proposed ASNs as well suited to RC,[7] due to their physically recurrent structure, useful feed-forward properties, and capacity for higher harmonic generation[1]. As a proof-of-concept, we have successfully validated network training of both our model and experimental system within the RC framework. This work represents a unified approach of experimentation and theory of complex systems to make ASNs a uniquely scalable platform for neuromorphic computing.

Selected Publications with MANA recognition:

1) A.V. Avizienis, H.O. Sillin, C. Martin-Olmos, H.H. Shieh, M. Aono, A.Z. Stieg, J.K. Gimzewski, *PLoS One* **7**(8), e42772 (2012).
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Atomic Electronics for Future Computing

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MANA Research Associate Takami Hino, Soumya R. Mohapatra, Qi Wang

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 beyond von-Neumann computers. 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.

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) Electrochemistry on the Atomic Level.[1]

Solid-electrochemical reaction is a phenomenon that has been known since the era of Faraday. It is also used in the operation of atomic switches to precipitate metal atoms and re-ionize them. Although the solid-electrochemical reaction is well understood and described in a form of a chemical equation, how it proceeds at the atomic scale has not been revealed.

We successfully achieved an observation of the solid-electrochemical reaction with atomic resolution by scanning tunnelling microscopy, which was enabled by doping of small amount of Fe ions into a super-ionic conductive material ($RbAg_4I_5$).

The experiment revealed that precipitation of metal atoms due to the reduction process of solid electrochemical reaction requires a certain time (time-lag) after bias application (Fig. 1). It was also revealed that a bias larger than a certain threshold value makes the time-lag negligible small. These phenomena do not appear in the chemical equations. This work was achieved in collaboration with a group of RWTH Aachen.

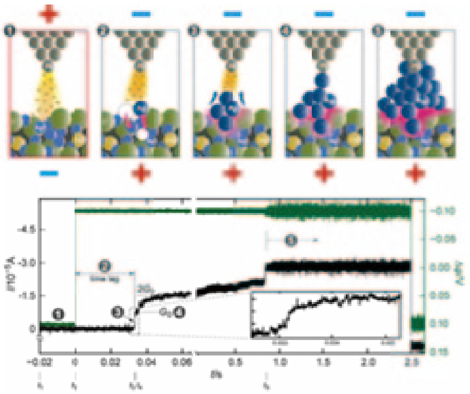

Fig. 1. Schematic of a solid-electrochemical reaction (a), and an experimental result showing a time-lag (b).

(2) New Functions in Gapless Atomic Switches.

We have developed new functions in gapless atomic switches. Using $Ag/Ta_2O_5/Pt$ gapless atomic switch, synaptic operations, such as achieved in a gap-type atomic switch[2] was demonstrated.[3] In the demonstration, we also confirmed that the operation of the gapless atomic switch is based on a metal filament formation by observing conductance quantization (Fig. 2).

We demonstrated multifunctional operations in a single device, just by controlling a local migration of oxygen ions in WO_{3-x}. Volatile and nonvolatile rectifications as well as bipolar resistance switching behaviors were attainted on-demand.[4] The multi- functionality will enable developments of conceptually new computers such as reconfigurable neural computing systems.

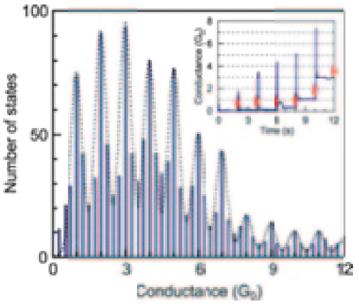

Fig. 2. Histogram of conductance-state showing conductance quantization, and observed stepwise change in conductance (inset).

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Braiding Majorana Fermions in Topological Superconductor

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NIMS Postdoctoral Scientist	Munehisa Matsumoto, Madhavprasad Ghimire, Bin Xi
Graduate Student	Yuki Takahashi, Feng Liu, Zhao Huang, Long-Hua Wu

1. Outline of Research

Topological quantum computation (TQC) is attracting considerable interests due to the unique feature of fault tolerance, where quantum information is stored non-locally and robust against decoherence caused by interaction with environment. Ground state degeneracy and rotations within the degenerate subspace with unitary non-Abelian transformation are the two important ingredients for its implementation. Systems with Majorana fermions (MFs), particles equivalent to their antiparticles, as zero-energy excitations are promising, since they are half of conventional Dirac fermions and can form non-local qubits. Superconductivity is a hopeful host for these zero-energy MFs where Bogoliubov quasiparticles are composed by both electrons and holes.

Activities in searching MFs in superconducting systems began with the intriguing illustration that a vortex in chiral p-wave superconductor can accommodate a zero energy MF at its core in an infinite system. It was then proposed that the same physics can be realized in a heterostructure of conventional s-wave superconductor (S) and topological insulator (TI). This idea was pushed forward that a spin-orbit coupling semiconductor (SM) in proximity to a ferromagnetic insulator (FI) plays a similar role as TI, and thus a S/SM/FI heterostructure can be a generic platform to provide the topological phase. Fantastically, it has been revealed that winding two vortices carrying MFs at their cores yields the non-Abelian statistics. Despite of its conceptual importance, realization of this idea seems unrealistc since vortices are hard to be manipulated at will.

In parallel to the search of MFs associated with vortex state, significant attentions have also been paid to MFs at the ends of one-dimensional (1D) spinless superconductor. This model system can be realized in a 1D spin-orbit coupling semiconductor under a magnetic field and in proximity to an s-wave superconductor. Non-Abelian braiding of end MFs has been discussed in several theoretical works. The idea is to drive end MFs by tuning gate voltages along the whole nanowires, which may harm the stability of the MFs.

2. Research Activities

(1) Manipulating edge MFs.[1)]

We have investigated finite samples of SM/FI heterostructure placed on a common superconducting substrate; samples are connected by constriction junctions; one superconducting vortex is pinned at the center of each SM/FI sample (Fig. 1). We have revealed that edge MFs can be prepared, transported and braided merely by application of point-like gate voltage at junction positions. In contrast with previous proposals, no delicate request on the gate voltage is necessary in the present scheme since it is used to turn off electron hopping among samples. The dynamics of edge MFs is monitored by solving the time-dependent Bogoliubov-de Gennes equation, and the non-Abelian braiding of MFs is confirmed. The present proposal provides a good way to manipulate topological qubits based MFs.

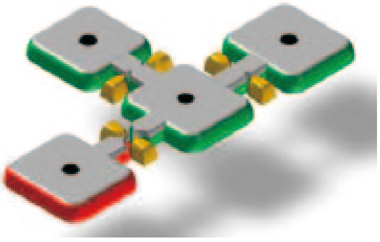

Fig. 1. Schematic device setup for generating and braiding edge MFs by tuning gate voltage at constriction junctions.

(2) Multi-component superconductivity with time-reversal symmetry breaking.[2)]

We have studied superconductors of more than three components with mutual repulsive forces caused by electron Coulomb interaction. Competition between the components produces a frustrated superconducting state characterized by nontrivial phase differences among superconducting components. As the result, time-reversal symmetry (TRS) is broken in the superconductor, yielding a pair of states with opposite chiralities (Fig. 2). The relative phase oscillation called Leggett mode becomes soft at the boundary between two states with broken and preserved TRS, which gives birth to a zero-energy collective excitation. It turns out that some puzzling experimental results for the low-temperature electronic specific heat of iron-based conductors can be explained by this zero-energy Leggett mode, implying the existence of the novel superconducting state characterized by TRS breaking. This novel superconducting state is also expected to have important applications such as new implementation of qubits and high-accuracy SQUID.

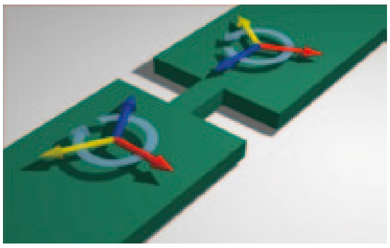

Fig. 2. Pair of superconducting states with broken time-reversal symmetry characterized by nontrivial phase differences.

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Surface Atomic Scale Logic Gate

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MANA Research Associate Maricarmen Grisolia, Demetra Piachos,
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1. Outline of Research

Design & construct of atomic scale calculators requires:

- The quantum design of a molecule (atom surface circuit) able to perform alone the logical operations.
- The molecule synthesis or/and atom by atom UHV-STM surface atomic scale circuit construction.
- The development of a surface multi-pad interconnection technology with a pm precision respecting the atom by atom order of the surface nano-system assemblage.
- The improvement of quantum chemistry software like N-ESQC to simulate the complete logic circuit with its interconnections and its supportive surface.

The CNRS Toulouse MANA satellite is working (i) on the interconnection of a single molecule logic gate and a DB circuit logic gate using DB wires or train of nano-gears, (ii) on the design of QHC logic gate and (iii) pursue the exploration of the atomic scale logic gate complexity roadmap to embed the maximum possible computing power inside a single molecule or a single surface atomic scale circuit.

2. Research Activities

(1) Logic Gate Architecture Theory for the Nanoscale.

We demonstrated that all the known intramolecular single molecule logic gate architectures: semi-classical circuits, quantum Hamiltonian circuits (QHC) and qubit circuits are different versions of the time dependant quantum control of intramolecular processes (Fig. 1). They only differ in the way the classical input data are encoded on the quantum molecular system and how the quantum to classical conversion proceeds to read the output. This had served to create better graph theory for QHC molecules[1)] and Fig. 2.

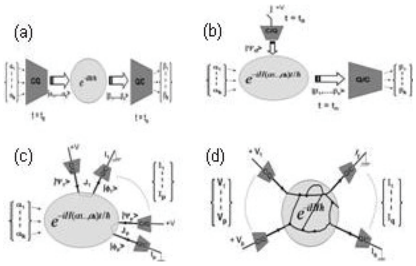

Fig. 1. The formal quantum logic gate circuit (a) qubit, (b) Population QHC, (c) Frequency QHC and (d) semi-classical circuit.

(2) Semi-Classical Logic Gates.

For surface atomic scale logic gates, dangling bond (DB) surface atomic wires are constructed using atom by atom vertical manipulation on a semi-conducting surface. Three surfaces are studied by the Toulouse MANA satellite: MoS_2, Si(100)H and Ge(001)H. For MoS_2, very details STS of S extracted atoms have been recorded in NIMS in collaboration with Toulouse depending on the number of S atoms extracted in preparation of surface logic gate construction.[2)] For Si(100)H, we focused on the stability of long DB wires where the AFM relaxation is the ground state as compared to the FM or Peierls surface structure.[3)] For Ge(001)H, it was shown experimentally and by calculations how the DB wire band electronic structure is formed depending on the number of H extracted.[4)]

For semi-classical molecule-logic gates, the detail interactions between the vibrations modes and through electron transfer processes were theoretically explored. It was shown that a vibronic resonance can exist between an electron transfer process and a polaronic like propagating deformation.[5)] This can speed up the rate of electron transfer through the surface polymerized PDA molecular wire obtained at NIMS. Unfortunately, this resonance is very fragile and will not support insertion like Zn Phtahalocyanine molecules along a PDA wires.

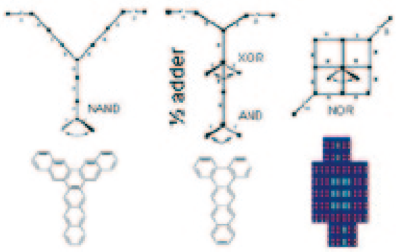

Fig. 2. A new quantum graph theory: molecule NAND, molecule ½ adder and DB NOR QHC logic gates.

(3) QHC Logic Gates.

To improve the design of complex QHC molecule logic gate, a new quantum graph theory was discovered starting from a simple topological Huckel theory to analyze the eigenvalue repulsion effect as a function of the end group hybridization. Using this theory, new conjugated molecules were designed reaching the complexity of an ½ adder molecule gate inside a molecule 1.4 nm in spatial expansion (Fig. 2). This is the smallest ever designed complex molecule logic gate giving the same truth table that the 6 transistors of a standard nano-electronic ½ adder. For the input latch, the physics of a train of nanogears ending by a molecule gear is starting to be studied experimentally to control the input chemical groups hybridization with the QHC calculating unit: a pentacene push-button surface latch, a surface pivoting acetophenone or a rotating molecule for surface DB Si(100)H NOR QHC logic gates (Fig. 2).

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Integration of Nano Functionality for Novel Nanosystems

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1. Outline of Research

We develop novel techniques and methodologies toward the realization of novel nanosystems for future information technology. Development and application of multiple-probe scanning probe microscopes (MPSPMs), manipulation of individual atoms and molecules, fabrication of low-dimensional nanostructures and measurements of signal transfer through neuromorphic network systems, are explored for a common purpose; creation and characterization of elemental nanostructures and functional nanosystems which transmit and transduce electrical, optical, mechanical, ionic and magnetic signals.

MSPM has simultaneously and independently controlled 2 to 4 scanning probes[1,2] which are brought into electrical contact to a single nanostructure and reveal its electrical property.[2,3] We have implemented atomic force microscope functions in our MSPM[4,5] and realized measurements of electrical properties of conductive nanostructures on insulating substrates.[2]

Fabrication of nanostructures and nanomaterials is an important part of our research towards a realization of functional nanosystems. For example, we believe that neuromorphic architecture changes the present computing technology and that our MPSPMs are not only suitable for investigating such architectures but also for controlling functions of them. Therefore, we also study how to construct neuromorphic network nanosystems.

2. Research Activities

(1) Multiple-probe Atomic Force Microscope.[2,4,5]

We have developed a multiple-probe atomic force microscope (MPAFM)[5] for conductance measurements of nanostructures on insulating substrates.[2] Based on this MPAFM, we have designed and constructed a new compact MPAFM installed in a desk-top scanning electron microscope (Fig. 1a). Since the electron gun can easily be removed and swapped with optical microscope, this new MPAFM system can measure various samples both in vacuum and in aqueous environments. The MPAFM adopts 5 piezo actuators for controlling positions of four probes and a sample in addition to newly designed large-stroke compact XYZ sliders as illustrated in Fig. 1b.

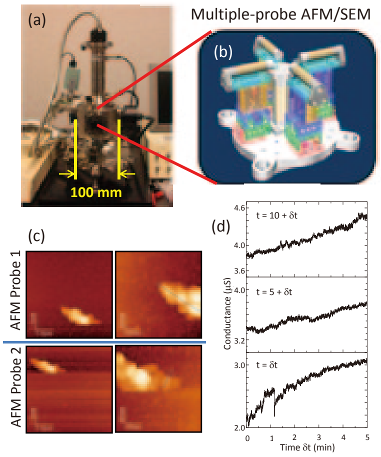

Fig. 1. Newly developed MPAFM/SEM system (a) and schematic view of MPAFM (b). A small network of CNHs aggregate is imaged by two of the MPAFM probes (c) and an evolution of a network is measured using MPAFM (d).

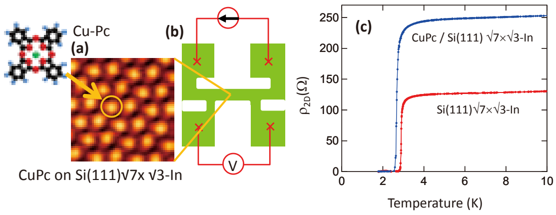

Fig. 2. Si(111)√7x√3-In covered with CuPc molecules (a) and a van der Pauw geometry (b). Zero resistance clearly appeared even the Si(111)√7x√3-In reconstructed surface is covered with a monolayer of CuPc molecules (c).

(2) Nanomaterials Research.[6-9]

To utilize interesting property of individual carbon nanohorns (CNHs) aggregates, i.e., pressure- dependent reversible and irreversible conductance evolution, a network of CNHs aggregates was formed and the whole conductance of the network was found to be affected by irradiating light or by flowing current through the nanosystem. Individual CNHs aggregates in a network are imaged with the new MPAFM (Fig. 1c) and the evolution of network conductance is measured using two AFM probes of the MPAFM in Fig. 1d.

We have also succeeded to develop multilayered silicene[8] for the purpose of MPAFM measurements to clarify intrinsic conductance of silicene where Si atoms form graphite like structure. After forming a capping monolayer with copper phthalocyanine (CuPc) molecules (Fig. 2a) on a Si(111)√7x√3-In reconstructed structure, we performed van der Pauw measurements at low temperatures in UHV (Fig. 2b) and found that superconducting current through the atomically thin superconducting system[9] still survives as shown in Fig. 2c. This would be an important step to use atomically thin superconductor for further processing toward a practical device fabrication.

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Mesoscopic Superconductivity and Quantum Information Physics

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1. Outline of Research

Our research topic is so-called mesoscopic super- conductivity which aims to explore new quantum phenomena in different kind of superconducting devices and to apply them to quantum information physics.

We are now developing an ultimate SQUID (Superconducting Quantum Interference Device), i.e., a nano-SQUID which can detect single or several spins. We will also clarify the quantum interaction between a nano-SQUID with embedded quantum dots and spins in dots. 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.

We are also working on superconductor-based Light Emitting Diode. 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.

Our other research targets are (i) transport of self-assembled InAs nanoring and (ii) chiral p-wave hybrid SQUID.

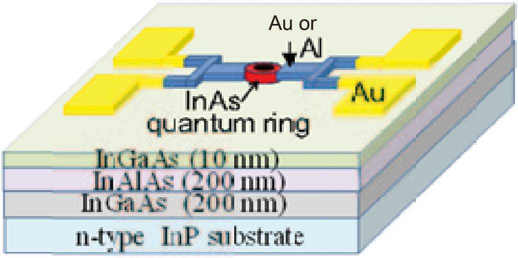

Fig. 1. Schematic view of the sample.

2. Research Activities

(1) Transport of Self-assembled InAs Nanoring.

We measured self-assembled InAs ring grown from 4 monolayer in droplet on InP non-doped substrate (Fig. 1). The ring showed superconducting characteristics. This is originated not from the proximity effect of Al electrodes but from residual In filament. The outer diameter, inner diameter, and width of the ring are about 120 nm, 38 nm and 40 nm, respectively. The measured differential resistance in a low bias regime as a function of applied magnetic field showed clear oscillations with a period of 0.326 T at magnetic fields over 1.8 T. This oscillation corresponds to *h*/2*e* oscillation. However, below 1.8 T no oscillation was observed. This means that the phase is not well defined below 1.8 T and possibility of quantum phase fluctuations in one-dimensional superconductor that result in quantum phase slip. The theory of one-dimensional superconductor with a quantum phase slip center shows peak splitting of the tunnel current peaks. Fig. 2 shows the measured tunneling current and clear peak splitting of the current peak. This indicates the existence of quantum phase slip in our nanoring.

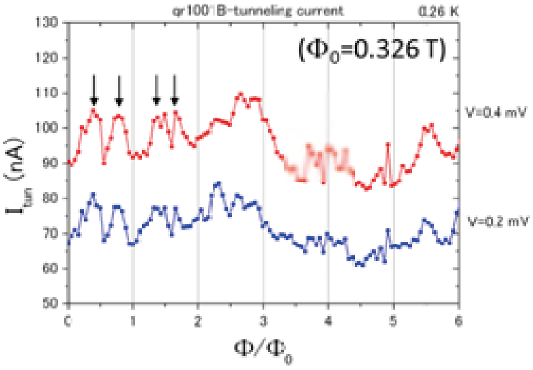

Fig. 2. Tunneling current as a function of magnetic field.

(2) h/4e Periodicity and the Time-Reversal Symmetry-Breaking in Supercurrent of a Chiral p-wave Hybrid SQUID.

We have fabricated a hybrid SQUID with narrow channel of a chiral p-wave superconductor Sr_2RuO_4 and measured interference patterns of magnetic fields and Shapiro steps under micro wave irradiation. Both dc and ac Josephson effect show the existence of h/4e periodicity. The origin of the h/4e periodicity is sin2Θ current of a chiral domain junctions which is different orbital angular moment of the cooper pair. And the existence of sin2Θ term makes clear time reversal symmetry breaking of the supercurrent of Sr_2RuO_4 (Fig. 3).

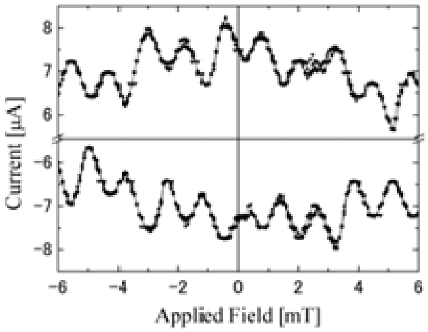

Fig. 3. An evidence of broken time reversal symmetry. There is a clear asymmetry between positive and negative critical currents.

In Situ Purification to Eliminate the Influence of Impurities in Solution-Processed Organic Crystals for Transistor Arrays

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Post-doc Yun Li

1. Outline of Research

One of the major factors driving the fast growth of the semiconductor manufacturing industry is a steady decrease in production costs. For traditional semiconductors, most of the cost originates from infrastructure, equipment, and processing. In contrast with low-cost strategies involving organic semiconductors, the materials can easily become one of the greatest costs. Here, we demonstrate a simple and efficient fabrication process, which involves in situ purification via spin-coating from organic semiconductor/polymer blends, to eliminate the influence of impurities on the electrical properties of the semiconductor. Thus, we achieve the same performance using low-purity, low-cost materials for transistor arrays with patterned organic semiconducting crystals as that obtained from high-purity materials. The exclusion of impurities is attributed to the vertical phase separation and crystallization that occur during spin-coating, which produces purified organic semiconducting crystals. With this reduction in cost, our results can redirect organic electronics to seek the lowest purity and lowest cost material that still provides adequate performance, rather than simply using the highest purity and costliest materials.[1-3]

2. Research Activities

In our experiment, we introduce a simple and solution-processed approach to pattern the surface wettability by using hydrophobic dielectrics and to produce the large plate-like organic crystals within the patterned regions. A mixture solution of organic semiconducting small molecule (C8-BTBT) and insulating polymer (PMMA) was spin-coated onto a substrate with patterned surface wettability. Organic crystals, which are selectively located on PMMA layer in self-assembling separation, were formed within the patterned regions without any post treatment. Large grain crystal (typical size ~hundreds of micrometers) are obtained. High device performance and uniformity were obtained from the fabricated transistor arrays on paper substrate with rough surface, exhibiting the field-effect mobility more than 1 cm^2/Vs and the on/off ratio of 10^8 (Fig. 1).

We also found a self-purification behavior in our double-layer structure owing to phase separation (Fig. 2). Even though we used as-synthesized semiconductor molecules containing the byproduct, the plate-like crystal transistor did not show any difference between the purified material and non-purified material. This could be explained as the in-situ purification to eliminate the influence of impurities in crystal transistor (Fig. 3).

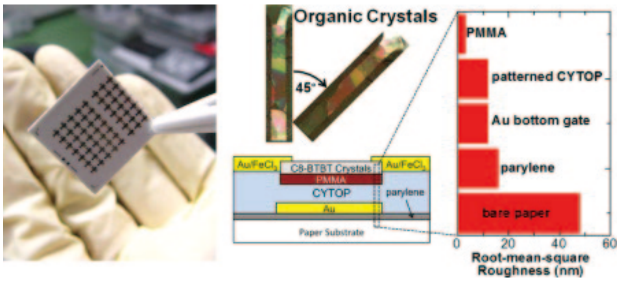

Fig. 1. **(Left) Field-effect transistor fabricated on paper substrate with solution-processed organic crystals confined in patterned regions. (Center) Schematic of organic transistor with self-phase between organic crystal channel and insulator polymer substrate. (Right) Root-mean-square (rms) roughness of the different surfaces from the bare paper substrate to the PMMA layer.**

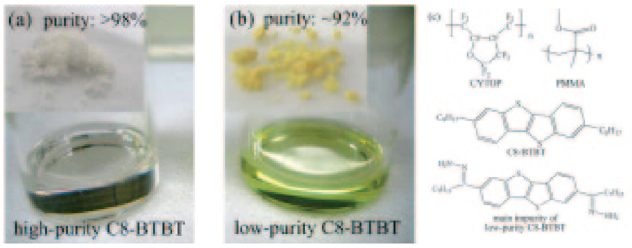

Fig. 2. **Optical images of the C8-BTBT solutions made with high- (a) and low purity (b) C8-BTBT. Insets show the high- (a) and low-purity (b) C8-BTBT powders. (c) Chemical structures of the materials used and the main impurity in low-purity C8-BTBT.**

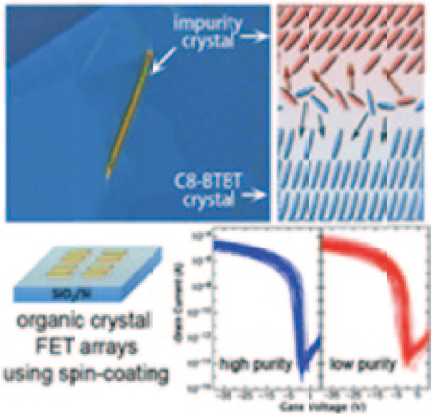

Fig. 3. **(Upper left) Cross-polarized microscopy image of the small needle-like crystal. (Upper right) illustration of the "in situ purification" during spin-coating with impurity (red ellipsoids) and C8-BTBT (blue ellipsoids) molecules. (Lower) Schematic of transistor array, and transfer curves of the FET arrays based on patterned C8-BTBT crystals from high- and low-purity materials.**

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

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1. Outline of Research

One of the most challenging problems for chemists/ material scientists is construction of efficient energy/ materials conversion systems. 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, non-linear spectroscopy, and x-ray techniques of the structure and functions of the interfaces as well as theoretical study are carried out so that structure-function relations should be established and rational design and construction of the desired interfacial phases become possible. Specifically, we have carried out 1. construction of catalytic interfaces by arranging atoms on metal surfaces in ordered manner, 2. construction of photoenergy conversion interfaces by forming ordered molecular layers on metal and semiconductor surfaces, and 3. experimental and theoretical investigations of structure and electron transfer processes at solid/liquid interfaces.

2. Research Activities

(1) Construction of catalytic interfaces by atomically ordered modification of metal surfaces.

Development of highly efficient multi-functional electrocatalysts attracted considerable attention be- cause of their important applications for interfacial energy conversion. Cataly- tic activities depend on the composition and structure of the catalysts. For example, the atomic ratio giving maximum catalytic activity for electrochemical methanol oxidation reaction, which is one of the most important reactions in fuel cell, is suggested to be $Pt_{50}Ru_{50}$. It is, however, not easy to prepare the catalysts with precise atomic arrangement. Usually two metal complexes are mixed together and decomposed thermally to obtain alloy. In this case, bulk ratio can be controlled but not nano-scale arrangement at the surface where reactions take place. We have proposed a new method, in which multi-nuclear metal complex is adsorbed on a substrate and then decomposed thermally so that atomically arranged nano- alloys can be formed and already demonstrated that Pt-Ru and Pt-Ni complexes are adsorbed on a Au (111) electrode surface in ordered manner and subsequent decomposition of the adsorbed species by heating followed by electro- chemical treatment resulted in highly dispersed PtRu[1] and PtNi particles, respectively, on the surface with very high electrocatalytic activity for methanol oxidation. This year we have found that Pt-Ru alloy prepared from Pt-Ru complex showed not only higher activity but also higher durability for methanol oxidation reaction than Pt-Ru alloy prepared from mixture of Pt and Ru chlorides (Fig. 1).

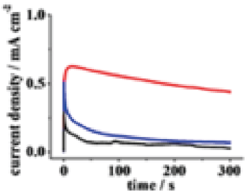

Fig. 1. **Current decay curves of Pt (black), Pt-Ru alloys prepared from Pt-Ru complex (red) and Pt and Ru chlorides (blue) in 0.1 M $HClO_4$ solution with 1 M methanol.**

Nitrogen doped carbon nanostructures are known to have effective metal free ORR catalyst, although the activity is still limited. We have shown both theoretically[2] and experimentally that BN thin film deposited on Au electrode is an effective ORR catalyst.

(2) Photoenergy Conversion at Metal and Semiconductor Surfaces Modified with Ordered Molecular Layer.

It is very important to produce hydrogen from water and It is very important to produce hydrogen from water and form useful compounds by reducing CO_2 using solar energy. We have already reported that visible light induced up-hill electron transfer at porphyrin-ferrocene thiol modified gold electrode is enhanced by the placing gold nano particles, which acted as plasmonic photon-antennas, on the molecular layer[3] and Pt complexes attached within molecular layers with viologen moiety, electron relay, formed on Si(111) electrode surface, Pt-V^{++}-Si(111), act as a "confined molecular catalysts" for photoelectrochemical hydrogen evolution reaction (HER).[4] This year we found that highly efficient and selective photoelectrochemical CO_2 reduction takes place at p-type Si(111) electrodes modified by molecular layer with viologen moiety and various metal complexes as shown in Fig. 2,[5] although HER is dominant at Pt metal electrodes. This shows unique behavior of "confined mole- cular catalyst".

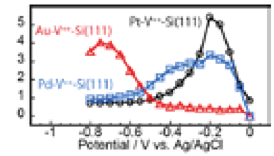

Fig. 2. **Ratio between photocurrents in Ar and CO_2 saturated 0.1 M Na_2SO_4 solutions at p-type Si(111) electrodes modified by molecular layer with viologen moiety and Pt (black), Pd (blue) and Au complexes (red).**

(3) Experimental and Theoretical Investigations of Structure and Electron Transfer Processes at Solid/liquid Interfaces.

One of the major goals in surface chemistry is to obtain a microscopic understanding of surface reaction at molecular level and time-resolved vibrational spectroscopy is one of the most powerful tools to investigate ultrafast reaction dynamics and to probe the transient state of adsorbates at surface. This year we studied the initial excited interfacial structure of dye sensitized solar cell system to understand the excited interfacial structure of dye/semiconductor in- terface in solution by fs visible pump IR probe technique (Fig. 3).

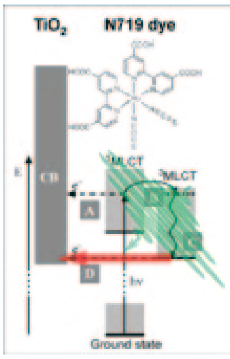

Fig. 3. **Electron injection takes place from ^{3}MLCT to conduction band of TiO_2.**

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Solid-State Batteries

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1. Outline of Research

Lithium batteries have been powering portable electronics including cellular phones and note PC's for more than 20 years. In addition, now they are expected to play new roles for realizing a low-carbon society as power sources in electric vehicles and energy storage device in smart grids. However, the safety issue arising from their combustible organic electrolytes remains unsolved.

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

2. Research Activities

(1) High-rate growth of $LiCoO_2$ epitaxial films.[1]

Battery performance is governed not only by bulk properties of the battery components but also by their interfaces. For example, our previous study revealed that space-charge layer formed at the interface can be highly-resistive and rate-determining. Deep insights into ionic conduction at such a hetero-interface will be gained from an ideal interface model, which is formed between orientation-controlled ionic conductors and into simple geometry, e.g. from epitaxially-grown thin-films of battery materials with atomically-flat surface.

We already succeeded in epitaxial growth of single crystal $LiCoO_2$; however, the deposition rate was very low. On the other hand, because the capacity of secondary battery is proportional to the volume of the active material, it is very important to investigate the electrode properties in thick-film electrodes. Although high fluence ablation increases the deposition rate, it causes composition deviation in the film. In this study, the deviation is compensated by controlling target composition and gas pressure, which results in the high deposition rate and high crystallinity (Fig. 1).

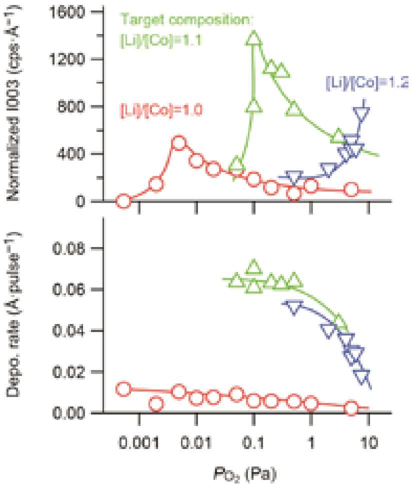

Fig. 1. P_{O_2} dependence of $LiCoO_2$ 003 peak intensity (upper) and deposition rate (lower).

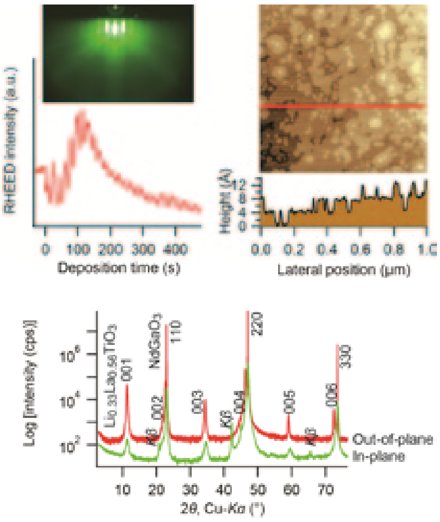

Fig. 2. RHEED intensity variation at the initial stage of epitaxial growth of $Li_{0.33}La_{0.56}TiO_3$ on a $NdGaO_3$ (110) substrate (upper left), a RHEED pattern from the substrate [010] direction (inset), an AFM image (upper right), and X-ray diffraction patterns (lower) of the resultant film.

(2) Epitaxial growth of $Li_{3x}La_{2/3-x}TiO_3$ films.[2]

Besides hetero-interface in electrodes, homo-interface between the battery-material particles can be rate-determining. For example, high grain-boundary resistance is a big issue especially in oxide-based solid electrolyte systems, even though some oxides exhibit fast ionic motion in the crystal lattice.

This study aims at epitaxial growth of $Li_{3x}La_{2/3-x}TiO_3$, which is a typical above-mentioned oxide-based solid electrolyte, in order to construct the ideal homo-interface. Moreover, the epitaxial film will reveal anisotropic ionic conduction, which has been expected in the material from the cation ordering, but has not been confirmed due to the absence of orientation controlled materials.

In this study, $Li_{3x}La_{2/3-x}TiO_3$ with $x \approx 0.11$ has been successfully grown on $NaGaO_3$ (110) substrates in a layer-by-layer manner, as shown in Fig. 2. The surface is atomically-flat with clear step-and-terrace structure, which is regarded as useful to construct ideal interfaces. Moreover, the strong (001) orientation of the film is helpful to investigate the anisotropy in the ionic conduction.

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Reticular Materials

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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. In this project so far, we have develop a conceptually new synthetic methodology to create metal complex arrays with controlled number, nuclearity, or sequence of metal centers (Fig. 1).[1–4] This methodology is now opening 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.

2. Research Activities

(1) Studies on the Secondary Structures of MOCAs and Related Species.[5]

Considering that the multimetallic species prepared by our methodology (Metal–Organic Complex Arrays; MOCAs) possess a peptide backbone, one of the important next challenges could be the control of 3D orientations of metal complexes in these arrays by means of spontaneous folding of peptide backbones into particular secondary structures (Fig. 1).

As the first step of this research, we investigated the secondary structures of several polypeptides bearing multiple chelating ligands, where, based on their CD spectral patters, amino acid sequences proper to form *α*-helix, *β*-sheet, and *β*-turn structures have been founded. For example, a trimer of alanine–tyrosine dipeptide sequence bearing a terpyridine ligand at the every tyrosine side chain, exhibits a CD pattern typical for *β*-sheet structure forming peptides. When the chain length of the peptide backbone was extended up to the corresponding decamer, its CD pattern suggested that the peptide rather adopted a *β*-turn structure. In sharp contrast to these examples, increase of alanine content in the peptide backbone to give a trimer of alanine–alanine–alanine–tyrosine bearing a terpyridine ligand at the every tyrosine side chain changed the peptide conformation into α-helix. In spite of the metallation of all the terpyridine ligands with Ru(II), the CD pattern was almost intact, suggesting that secondary structures observed for the peptide sequences could be retained in the case of corresponding MOCA species.

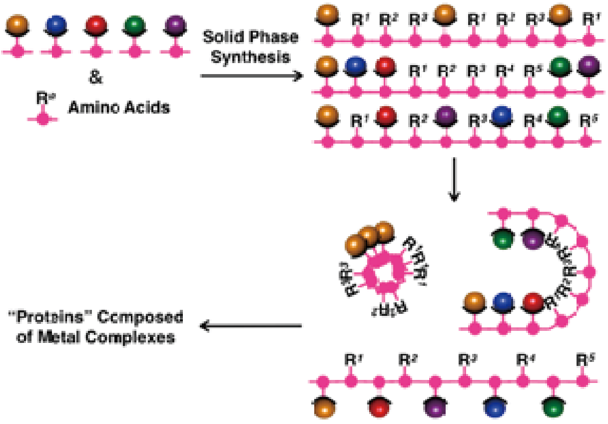

Fig. 1. Schematic representation of the control of 3D orientations of metal complexes in MOCAs by means of spontaneous folding of peptide backbones into particular secondary structures.

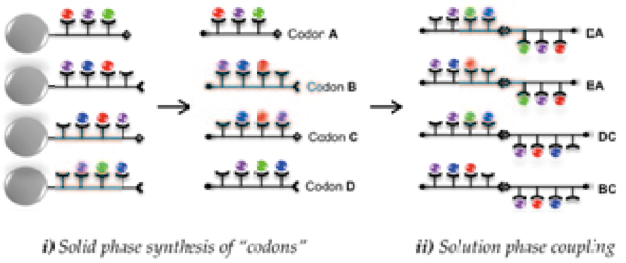

Fig. 2. Schematic representation of Solid-Phase Synthesis Coupled with Post Reactions in Solution Phase.

(2) Coupling of Solid-Phase Synthesis with Post Reactions in Solution Phase.[6]

In general, reactions on the polymeric resins for the solid-phase synthesis take place less efficiently than those in homogeneous solutions, which often limits the accessible length of the polypeptide chains in the case of solid-phase polypeptide synthesis. One of the solutions for this issue is the combination of solid-phase synthesis of peptide oligmers with their successive solution-phase coupling. We tried this approach for the preparation of longer MOCAs (Fig. 2) and eventually confirmed the formation of MOCAs composed of, *e.g.*, 10 metal centers from 5 different types of metal complexes.

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Nanoarchitectonics of Hybrid Artificial Photosynthetic System

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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 interactions between photon, carrier, molecules, and manipulation of these interactions 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 theoretical 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.

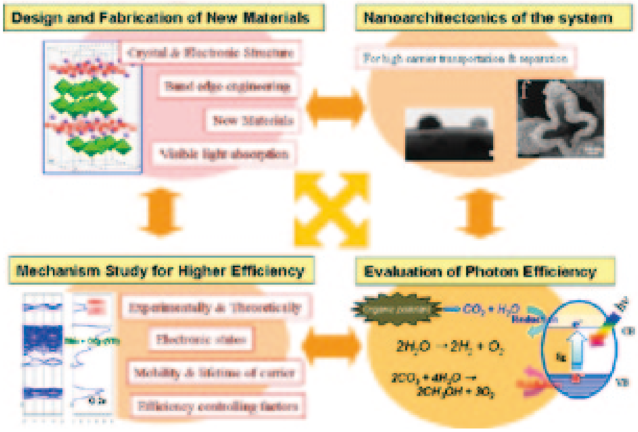

Fig. 1. Four sub-themes and their organic coordination for conducting effective materials exploration research.

2. Research Activities

(1) A new strategy for promoting photocatalytic water splitting via modulating reaction-environment.[1)]

We found that surface alkalinization induced by a high alkalinity of the solution environment can significantly shift the surface energy band of $SrTiO_3$ photocatalyst to a more negative level, supplying a strong potential for H_2O reduction and consequently promoting the photocatalytic efficiency of H_2 evolution to a quantum efficiency as high as 25.6% under visible light irradiation (Fig. 2).

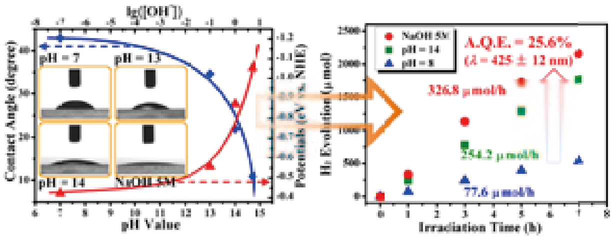

Fig. 2. Reaction-environment modulation enhances the H_2 evolution over $SrTiO_3$-based Photocatalysts.[1)]

(2) Efficient conversion of CO_2 to CH_4 fuel by oxide photocatalysts.[2-5)]

We have developed several oxide photocatalysts which own enough negative conduction band potentials, and hence can successfully convert CO_2 into CH_4 fuel under light irradiation.[2-5)] Especially, we have revealed that controlling surface oxygen deficiency is critical in carbon dioxide reduction reactions (Fig. 3).[2)] An extensive study from both experimental and theoretical approaches demonstrated that the enhanced catalytic activity is resulted from oxygen deficiency-related synergistic effects on the visible light absorption and the carbon dioxide adsorption properties of the catalyst surface. The result provides important guideline for developing highly efficient catalysts.

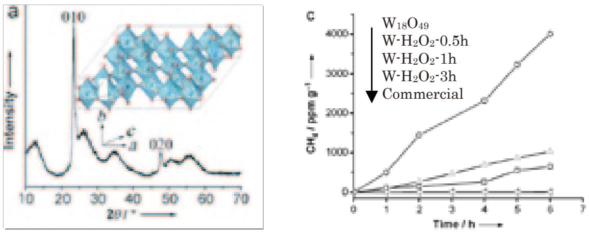

Fig. 3. A) XRD pattern and crystal structure of oxygen deficient WO_3 nano-wires. C) Time courses of CH_4 production over the tungsten oxide samples with different oxygen-vacancy concentrations, introduced by treatment with H_2O_2 for different time.[2)]

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Smart Nano-Biomaterials

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NIMS Junior Young-Jin Kim

1. Outline of Research

Smart polymers/materials, known as stimuli-responsive polymers/materials, have ability to changes in their properties because of stimuli-responsive property such as electric/magnetic field, temperature, pH or light. Among many smart polymers, the most widely employed smart polymer is a poly(N-isopropylacrylamide) (PNIPAAm) which show a thermally reversible phase transition from hydrophilic to hydrophobic through a lower critical solution temperature (LCST) around 32°C . Among many type of nanostructures, nanofiber is the most widely used structure because of their biomimetic structure, high specific surface area, high molecular alignment and high porosity compared to films or hydrogels. Electrospinning, the most widely employed method for preparation of nanofiber, is a versatile method of generating continuous nanofibers by applying an electrical charge to polymer solution.1) The diameter can be controlled by adjust electrospinning parameters such as concentration of polymer solution, distance between tip to collector, applied voltage and feed ratio.2) Of particular interest is smart nanofiber with stimuli-responsive properties which can be controlled by external stimuli. Despite of several studies on smart nanofibers using PNIPAAm, they are not stable in aqueous solution below the LCST. Here, as a solution of this problem that solubility of PNIPAAm nanofiber in aqueous solution, we studied the thermal-crosslinkable and temperature-responsive smart nanofiber, which have tunable properties by temperature alternation without any disperse or collapse in aqueous solution.3) Next, we demonstrated their potential for cancer therapy.

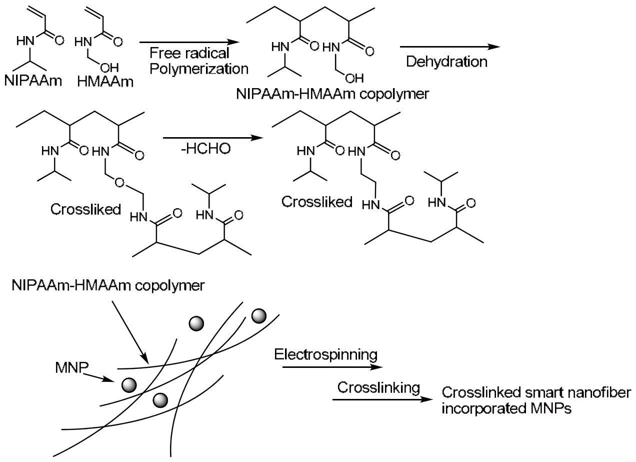

Fig. 1. Preparative scheme of nanofibers with MNPs.

2. Research Activities

To achieve this purpose, we have developed a novel self-heating and temperature-responsive nanofiber using magnetic nanoparticles (MNPs) because of their self-heating property by applying alternative magnetic field (AMF).4) Fig. 1 shows schematic representation of preparation of the nanaofibers. The poly(NIPAAm-co- hydroxymethyl acrylamide) (abbreviated as poly (NIPAAm-co-HMAAm) in hexafluoroisopropanol and MNPs in distilled water solutions were mixed in a 10/1 ratio for electrospinning and the resulting mixture was then subjected to voltage of 20 kV. The weight fractions of MNPs in the polymer were varied from 18-31 wt%. The nanofibers were randomly distributed (Fig. 2) to form the continuous fibrous structure with an average diameter of 350 nm by AFM measurement. Thermal crosslinking was carried out at 110°C for 7 h. The fibers preserved their morphology even after thermal crosslinking. Moreover, The MNPs were uniformly dispersed in the nanofibers.

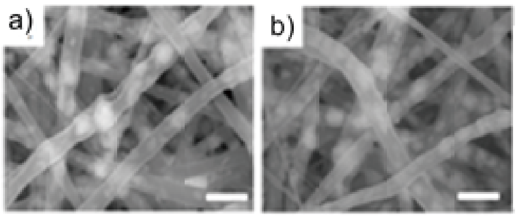

Fig. 2. SEM views of nanofibers with MNPs.

In hyperthermia, the control of generated heat is necessary for reduction of side effects. We checked the time-dependent heating of the nanofiber with different MNP compositions. For the nanofiber with 31 wt% MNP without crosslinking, the temperature increased from 4 °C to 29, 44, and 72 °C after 600 s for nanofibers with contents of 5, 15, 25 mg of the sample in 300 μL of PBS, respectively. For 31 wt% MNP after crosslinking, the temperature increased to 27, 32, and 46°C after 600 s for nanofibers with contents of 5, 15, 25 mg in 300 μL of PBS, respectively. Now, we are studying synergistic effect of chemotherapy and thermotherapy. Actually, both hyperthermia and DOX effects of the DOX/MNP-nanofiber in vitro are investigated by the evaluation of cytotoxicity to human melanoma cell line COLO 679 cells.

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Collagen Functionalization and Cellular Uptake of Single-Walled Carbon Nanotubes for Biomedical Applications

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1. Outline of Research

Carbon nanotubes (CNTs) have shown great potential for biological and medical applications because of their intrinsic unique properties. One of the most fascinating benefits of CNTs is the ability to efficaciously traverse biological barriers and enter even cell nuclei in an energy dependent or independent manner. Nevertheless, the applications of CNTs have been severely restricted by their super–hydrophobicity and easy aggregation in aqueous medium. The features are associated with cytotoxicity and other negative cellular effects, whereas well–dispersed CNTs show no apparent cytotoxicity. Therefore, stable CNT dispersion systems that retain the intrinsic CNT properties and have no or negligible negative cellular effects are desirable.

In this study, biocompatible collagen was used to functionalize single–walled carbon nanotubes (collagen–SWCNTs) to improve their dispersion in aqueous solution and cellular uptake.1) The effect of collagen–SWCNTs on the viability of bovine articular chondrocytes was analyzed by WST–1 assay and live/dead staining. The effect of collagen–SWCNTs on the mechanical property of chondrocytes was investigated by atomic force microscopy.2) The cellular uptake of collagen–SWCNTs was quantified through concentration–dependent ultraviolet–visible–near–infrared (UV–vis–NIR) spectroscopy. Distribution of collagen–SWCNTs in cells was investigated using confocal Raman imaging.

2. Research Activities

To improve the dispersibility in water, SWCNTs were functionalized with collagen using a simple non–covalent approach. Raman spectrum analysis showed a new peak at 1100 $\mathrm{cm^{-1}}$ resulted from the collagen backbone, confirming the modification of SWCNTs by collagen. The collagen–SWCNTs were individually dispersed in aqueous solution. The inherent properties of SWCNTs were retained after collagen functionalization and the collagen–SWCNT suspension solution was stable over 63 days.

The collagen–SWCNTs were added to the cell culture medium and their effect on cell functions of bovine chondrocytes was evaluated. The results of WST–1 assays on the metabolic activity (cell viability) of cell populations upon exposure to collagen–SWCNTs at a concentration of ≈ 15 μg/mL over time showed that no obvious differences were observed among the cells cultured with normal culture medium, medium supplemented with collagen or medium supplemented with collagen–SWCNTs during the 15 days of culture. The results indicated that collagen–SWCNTs at a concentration of ≈ 15 μg/mL did not affect cell viability. The viability of the cells was further confirmed by live/dead staining. Few red–stained cells were detected. Most of the cells were alive in all of the three culture conditions with or with collagen–SWCNTs. Type II collagen is a specific marker of articular chondrocytes. The expression of type II collagen indicates that the function of articular chondrocytes is maintained. In this study, cells cultured in all groups were positively stained with anti–collagen II antibody, indicating that the collagen–SWCNTs did not affect the capacity for expression of chondrogenic genes. The effect of internalized SWCNTs on cellular mechanical property was analyzed by using AFM to monitor the Young's modulus of chondrocytes after being cultured with SWCNTs.2) The cells cultured with SWCNTs showed significant higher Young's modulus at indentation depths of 200 nm and 500 nm than that of cells cultured without SWCNTs. The incorporated SWCNTs increased the Young's modulus of cells and the effect became more evident when the cells were indented at a high depth. These results indicated that the collagen–SWCNTs did not show any negative effects on the viability and gene expression of bovine chondrocytes, but increased cellular Young's modulus.

The cellular uptake amount of collagen–SWCNTs by the entire cell population increased over time and then remained stable after being cultured for 6 days. Up to ten million SWCNTs were internalized in one cell on average. Collagen-SWCNTs were retained in the cells for over a week, suggesting that the collagen–SWCNTs were cytocompatible and appropriate for CNT–based cell imaging and cell therapy. The enhanced uptake and prolonged dwell time of collagen–SWCNTs in cells should be attributed to the bioactive collagen on the surface of nanotubes. The high uptake of collagen–SWCNTs will facilitate their applications for SWCNT–based drug delivery, DNA transport, biological probing, intracellular imaging and cancer therapy.1)

Investigation of the time-course change of SWCNTs incorporated in cells and absorbed in ECM indicated that absorption of SWCNTs by the ECM could be an important step for the cellular uptake of the SWCNTs. Confocal Raman imaging showed that the distribution of collagen–SWCNTs in the cells was most prevalent in the perinuclear region. The high stability, easy cellular uptake and long retention in cells of the collagen–SWCNTs will facilitate the biomedical and biotechnological applications of SWCNTs.

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Nanotherapeutics Based on Redox Polymer Nanoarchitechtonics

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Post-doc Yukichi Horiguchi, Toru Yoshitomi

1. Outline of Research

The objective of our research is to create new bioactive materials for high performance therapeutic system. In order to use materials in vivo, interactions between materials surface and bio-components such as blood and tissue must be controlled. Non-biofouling surface is one of the most important characters for high performance biomaterials design. Using our surface constructing technique thus developed, we have developed novel bionanoparticles. Highly dispersion stable and biocompatible nanoparticle is known to increase its blood circulation tendency. In order to control these nanoparticles in vivo, we have to install further specific functionality via new concept by novel materials nanoarchitechtonics technique. In 2012, we have developed novel redox biointerface, redox nanoparticle for cancer therapeutics and redox polymer for Alzheimer's disease.

2. Research Activities

(1) Biointerface.

Various materials are employed in blood-contacting implantable and extracorporeal medical devices, such as artificial hearts, artificial blood vessels, hemodialyzers and apheresis columns. Since most of those medical devices have poorly biocompatible surfaces, anticoagulants are utilized to prevent thrombosis and embolism induced by contact between blood and these medical devices. Surface coating by biocompatible polymers such as poly(ethylene glycol) and dextran is commonly used to reduce biofouling significantly. Nevertheless, even today, all blood-contacting devices cause thrombosis with long-term usage. In fact, synthetic vascular grafts with inside diameters of less than 6 mm cannot be used because they are prone to early thrombotic occlusion. We have developed nitroxide radical-containing polymers (NRP), which strongly scavenge reactive oxygen species (ROS). When the NRP-coated beads were placed in rat whole blood, it decreased the generation of ROS and inflammatory cytokines, thus resulting in the suppression of blood coagulation (Fig. 1). On the basis of these results, NRP is anticipated to be a new blood-compatible material that attenuates the activation of blood cells and blood coagulation.

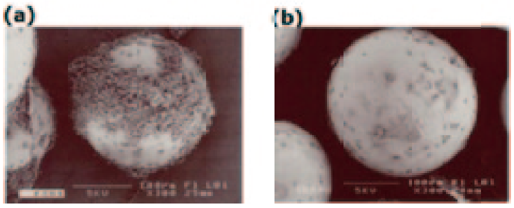

Fig. 1. TEM of glass beads contacted with whole blood without (a) and with (b) NPR coating.

(2) Nanoarchitectonics in vivo: Redox Cancer Therapeutics.

Despite years of anti-cancer drug development, including that of molecularly targeted therapeutics with their ability to selectively interfere with certain hallmarks of cancer, no perfect anticancer drug has been developed thus far. In recent years, chronic inflammation of the cancer microenvironment has been attracted considerable attention. For example, accumulated inflammatory cells such as macrophage and neutrophil generate reactive oxygen species (ROS) and inflammatory cytokines, which activate inflammatory transcription factors, such as nuclear factor-kappa B (NF-κB). Because the activation of NF-κB suppresses apoptosis of the tumor cells, it is considered to be one of the mechanisms to increase resistance for cancer chemotherapy. We have designed new adjuvant for cancer chemotherapy based on redox nanoparticle delivery system. We have prepared core-shell type nanoparticle by self-assembling amphiphilic block copolymer possessing stable nitroxide radicals in its core (abbreviated as RNP, Fig. 2). Several important points of our RNP-design are as follows: i) Since pH-disintegration character was introduced in RNP, the nitroxide radicals were exposed in acidic tumor environment, which was confirmed in vivo in this study; ii) RNP suppressed NF-κB activation of cancer cells, which was confirmed in vitro. iii) Intravenous administration of RNP prior to anticancer drugs scavenged ROS and suppressed oxidative stress in tumor environment and improves chemotherapeutic efficiency; iv) Long-term blood circulation of RNP suppressed adverse effect of cancer drug to normal organs, which was confirmed by cardiotoxic effect in vivo.

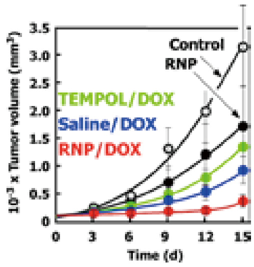

Fig. 2. Effect of RNP^{N} pretreatment on the antitumor activity of doxorubicin (DOX) in tumor-bearing mice (Animals were intravenously pretreated with RNP^{N} for 4 days, days -4 to -1). DOX was intravenously administered at a single dose of 10 mg/kg on day 0.

(3) Nanoarchitectonics in vivo: Nanotherapeutics for Alzheimer's disease.

Redox therapeutics was expanded to oral administration. When we orally administered pH-sensitive RNP to senescence-accelerated-prone mice, cognition completely recovered after 4 weeks. Pro-inflammatory cytokines and oxidative product markers were also effectively suppressed by oral RNP treatment, although acetylcholinesterase activity was not inhibited. Thus, oral administration of RNPs is a promising candidate as a novel redoc polymer therapeutics for dementia diseases.

Nanoarchitectonics-Driven Interfaces and Nanoparticles for Therapeutic Applications

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Post-doc (MANA) Y.T. Richard Lau

1. Outline of Research

Our research aims to provide diagnostic and therapeutic modalities of minimal invasiveness for eventual clinical use. One project explores the applications of engineered interfaces in cardiovascular therapies, using chitosan-phosphorylcholine (CH-PC), a non-toxic membrane-mimetic[1] derivative of the cationic polysaccharide chitosan previously used as supporting matrix for the survival and amplification of stem cells[2] and as vector in gene therapy.[3] Drug CH-PC conjugates were prepared and evaluated as coatings or as water-borne nanoparticles. In addition, we initiated a research project on the use of emerging inorganic nanoparticles in bio-imaging and nano-medicine.

2. Research Activities

(1) 17β-Estradiol Polysaccharide Conjugates for Cardiovascular Therapies.

The steroidal hormone 17β-estradiol (E2) is known to exert beneficial effects in the prevention and treatment of cardiovascular diseases. The cardiovascular beneficial effects of E2 result from cellular mechanisms that occur on the cell membrane, unlike the hormonal effects of E2 that take place in the cell nucleus. Hence, for maximum cardiovascular beneficial effects, E2 must be able to interact with membrane-associated estradiol receptors (ER) without activating the hormonal genomic effect. The selectivity of E2 for membrane ER was achieved by conjugating it permanently to CH-PC. This E2-conjugate (CH-PC-E2, Fig. 1A) forms thin films on hydrophilic substrates. Angle-resolved X-ray photoelectron spectroscopy (XPS) analysis of dried films (Fig. 1B) revealed a significant E2 enrichment of the topmost section of the film, attributed to the preferential migration of E2 towards the film/air interface upon drying (Fig. 1C). CH-PC-E2 films were rehydrated with a phosphate buffer saline in the sample compartment of a quartz crystal microbalance with dissipation (QCM-D). The QCM-D signals recorded upon injection of ER-α solutions (10 to 100 nmol) indicated that ER was adsorbed permanently on CH-PC-E2 films (Fig. 1C).[4] These studies are complemented by mechanistic investigations of the non-genomic pathways of E2 using micropatterned surfaces that expose cells to specific doses of E2 displayed on the interface (Fig. 1D).

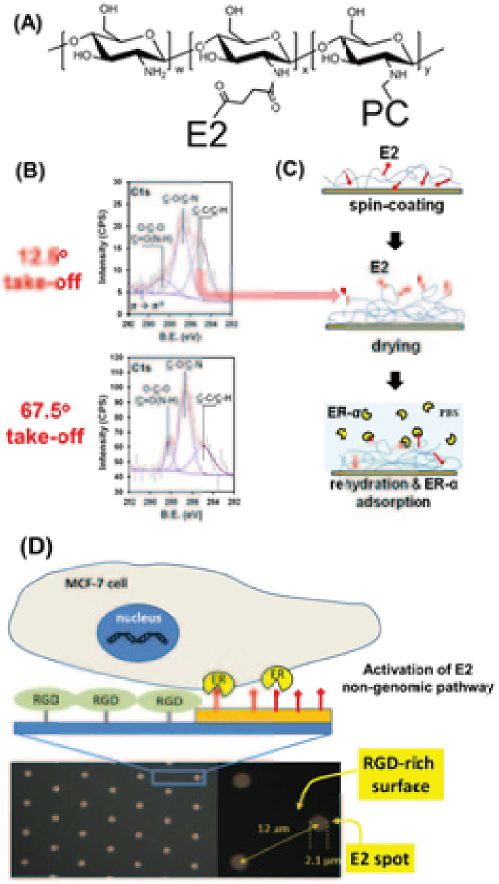

Fig. 1. **(A): Chemical structure of CH-PC-E2; (B): Depth-dependent XPS spectra of CH-PC-E2 films; (C): Morphology of CH-PC-E2 films and interactions with ER-α; (D): Micropatterned surface for mechanistic studies of E2 non-genomic pathways.**

(2) Emerging inorganic nanoparticles.

We initiated a study that explores applications in nanomedicine of emerging nanomaterials prepared within the WPI-MANA center. Emissive silicon and germanium nanoparticles (N. Shirahata) are assessed for *in-vitro* and *in-vivo* imaging as non-toxic alternatives to traditional cadmium-containing quantum dots.[5] Boron nitride nanotubes (D. Goldberg) coated with biopolymers are evaluated as drug delivery systems and as rheology modifiers for hydrogels and substrates for cell culture.

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Next-Generation Semiconductor Nanodevices

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1. Outline of Research

Nanoscale silicon devices using silicon nanowires (SiNWs) such as metal-oxide semiconductor field-effect transistors (MOSFETs) require properties that allow their electrical conductivity to be controlled. Considerable efforts have been directed for developing nanoscale silicon devices. Impurity doping of SiNWs or germanium nanowires (GeNWs)[1-3] is generally performed *in situ* during vapor-liquid-solid (VLS) growth, which has the advantage of not inducing defects. However, there are also certain disadvantages, such as surface doping and tapering structures created by sidewall growth, resulting in non-uniform doping along the growth direction of NWs.

On the other hand, ion implantation is now commonly used in semiconductor manufacturing. This technique allows the precise control of dopant concentration in the growth direction. In bulk Si, the introducing of dopant impurities and defects, their interaction, the recrystallization process with defect annihilation in implanted regions, and the subsequent reactivation process of dopant impurities have been extensively investigated. The recrystallization process with defect annihilation is a key point for controlling the reactivation and distribution of dopant atoms. Recently, ion implantation has been performed in SiNWs to fabricate p- and n-type SiNW.[4]

2. Research Activities

(1) Reactivation of B and P atoms in Si nanowires.

Raman scattering measurements were performed to investigate the the reactivation of B acceptor atoms in SiNWs by activation annealing (Fig. 1). After B ion implantation, the Si optical phonon peak significantly decreased. The intensity of the Si optical phonon peak increased gradually with increasing annealing temperature and almost recovered at 900 ˚C. In addition to this, the B local vibrational peak was observed at about 618 cm^{-1}, showing that the B atoms were doped in Si substitutional sites in the crystalline Si core of SiNWs during the recrystallization process. The intensity of the B local vibrational peak also increased with increasing annealing temperature. The Si optical phonon peak showed a broadening toward a higher wavenumber with increasing annealing temperature. This broadening is due to the Fano effect, showing the presence of a high concentration of holes, namely the reactivation of B atoms. Hence, these results clearly demonstrate the success of B doping by ion implantation. We also performed ESR measurements to investigate the reactivation of P atoms in SiNWs. After P ion implantation, the ESR signal of conduction electron signals with a g-value of 1.998 was observed, showing the activation of P donors in SiNWs.

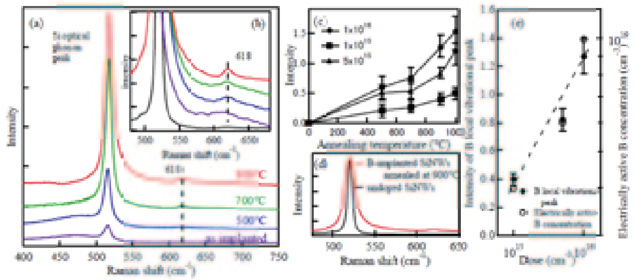

Fig. 1. (a) Si optical phonon peak and B local vibrational peak observed for SiNWs after B ion implantation and subsequent activation annealing. (b) Magnified image of (a). (c) Dependence of the intensity of the B local vibrational peak on the annealing temperature. (d) Change in Si optical phonon peak before and after implantation with a dose of 1 x 10^{16} B^{+}/cm^{2}. (e) Dependence of the intensity of the B local vibrational peak and the electrically active B concentration on the ion implantation dose.

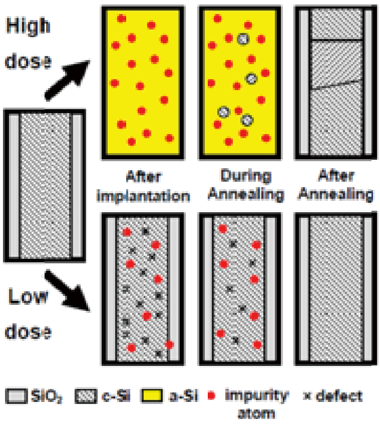

Fig. 2. Schematic of the recrystallization process of ion-implanted SiNWs by thermal annealing.

(2) Recrystallization of Si nannowires.

The recrystallization process of ion-implanted SiNWs by thermal annealing is shown in Fig. 2. The type of recrystallization closely depends on the implantation dose. High-dose implantation damages the crystal core and completely converts it to an amorphous state. Once the crystal Si core has been made amorphous, nucleation occurs randomly, resulting in the formation of polycrystal Si core on thermal annealing, since the initial crystal direction cannot be maintained. On the other hand, when the crystal Si core is only partially damaged, by low-dose implantation or hot implantation, the initial crystal direction is retained in the remaining crystal. Hence, nucleation readily occurs in the remaining crystal region as a result of thermal annealing, resulting in the formation of single crystals in SiNWs.

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Development of Nano Biomedicines

Group Leader **Nobutaka HANAGATA**
(Nano-Life Field)

1. Outline of Research

My challenge is to apply beneficial technologies to society by integrating original biological discoveries with original materials technologies and nanotechnology. The integration of life sciences and nanotechnology/materials science has two approaches. The first approach is to link critical knowledge in the life sciences to technological innovations through the use of nanotechnology and materials science. The other approach is to use nanotechnology and materials science to lead to important discoveries in the life sciences. To accomplish research using these two approaches, I use the following foundational technologies; global gene expression analysis, protein interaction analysis and bioimaging as fundamental technologies in life science, and manufacturing of nanoparticles, nanotubes and nano-patterned surfaces as fundamental technologies in materials science and nanotechnology.

2. Research Activities

(1) Development of natural CpG DNA drugs consisting entirely of phosphodiester backbone.[1)]

Unmethylated cytosine-guanine (CpG) motif-containing oligodeoxynucleotides (ODNs) have been well characterized as agonists of Toll-like receptor 9 (TLR9). In human, TLR9 is mainly expressed by B cells and plasmacytoid dendritic cells. ODNs with a phosphorothioate (PTO) backbone have been studied as TLR9 agonists since natural ODNs with a phosphodiester (PD) backbone are easily degraded by a serum nuclease, which makes them problematic for therapeutic applications. However, ODNs with a PTO backbone have been shown to have undesirable side effects. Thus, our goal was to develop nuclease-resistant, PD ODNs that are effective as human TLR9 (hTLR9) agonists. The sequence of ODN2006, a CpG ODN that acts as an hTLR9 agonist, was used as the basic CpG ODN material. The 3'-end modification of ODN2006 with a PD backbone (PD-ODN2006) improved its potential as an hTLR9 agonist because of increased resistance to nucleolytic degradation. Moreover, 3'-end modification with oligonucleotides showed higher induction than modification with biotin, FITC, and amino groups. Further, enhancement of hTLR9 activity was found to be dependent on the number of CpG core motifs (GTCGTT) in the PD ODN containing the 3'-end oligonucleotides. In particular, ODN sequences consisting of two to three linked ODN2006 sequences with a PD backbone (e. g., PD-ODN2006-2006 and PD-ODN2006-2006-2006) acted as effective agonists of hTLR9 even at lower concentrations. These CpG ODNs can be used as potentially safe agonists for hTLR9 activation instead of CpG ODNs with a PTO backbone.

(2) Development of intracellular delivery system for CpG DNAs.[2-4)]

Delivery systems for CpG ODN using nanoparticles as carriers differ greatly from delivery systems of other nucleic acid drugs such as antisense DNA and small interfering RNA (siRNA) for cancer treatment. For delivery of antisense DNA and siRNA, after they have been taken up by cells as a result of endocytosis, their nucleic acids must move from the endosome to the nucleus. However, with the delivery of CpG ODN, because the TLR9 is localized in the endolysosome, CpG ODN must be retained in the endolysosome for a long period of time. Therefore, delivery systems using CpG ODN require a design strategy different from conventional drug delivery systems. We have developed mesoporous silica nanoparticles, boron nitride nanoparticles and silicon quantum dot nanoparticles for CpG DNA delivery. The advantages of using these nanoparticles as CpG ODN carriers include protection from DNase degradation, decrease in the amount administered because cellular uptake efficiency is improved, the ability to change the structure of CpG ODN, the ability to deliver to target tissues, and the ability to slow-release CpG ODN over a long period of time.

(3) Safety and toxicity assessment on nanomaterials.[5,6)]

In recent years, products that include nanoparticles have increased drastically in recent years. However, no standards have been established concerning the safety of nanoparticles. From global gene expression analysis of cells exposed to nanoparticles, we are elucidating molecular mechanisms involved in nanoparticles' cellular toxicity.

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Bioactive Ceramics Materials

Group Leader **Masanori KIKUCHI**
(Nano-Life Field)

1. Outline of Research

Bioactive ceramics is divided into two types. One is conventional one that can directly bond with bone but not influences cell functions so much. Another type can activate target cell functions. We have been investigating both type of bioactive ceramics and ceramic/polymer composites for tissue regeneration. This year, we investigated hydroxyapatite/collagen bone-like nanocomposite (HAp/Col, Fig. 1) with properties that cell function activation and incorporating into bone remodeling process. In fact, the results of clinical tests of the HAp/Col porous body were reported by medical doctors and revealed excellent bone repairing ability at 20% higher than conventional ceramics in average. More excitingly, 75% of high efficacy ratio was reported for the HAp/Col porous body when repairing large bone defects in which 10-30 ml of materials needed to fill, even 0% of that for conventional ceramics.[1)] We have been continuing further improvement in its functionalities, injectable and safer gene transfer. In addition, to support practical use (commercialization) of new biomaterials, studies on bioactive ceramics evaluation methods for establishment of new international standards.

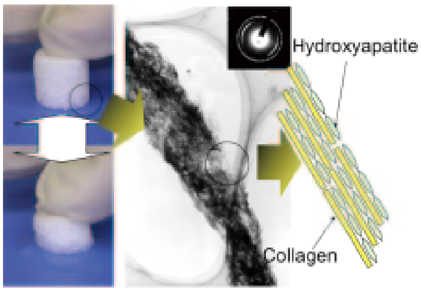

Fig. 1. Hydroxyapatite/collagen self-organized nanocomposite has nanostructure in which apatite and collagen are regularly aligned, and can be formed to sponge-like porous body.

2. Research Activities

(1) Injectable HAp/Col materials.

Injectable artificial bone with bioresorbability is strongly desired in practical medicine to realize good minimum invasive surgery to reduce potential risk of bone fractures as well as inhibition of new bone formation due to remaining of cements in body. Injectable HAp/Col could be good candidate. We utilize sodium alginate (Na-Alg) for gelation and lubrication agent for injectable HAp/Col. This year we investigated effect of additive in viscosity and anti-decay property. As an additive, one of organic acids or calcium compounds was added to the paste. Viscosity of the paste increased with increasing in additive amount; however, all pastes soaked in 37 °C phosphate buffered saline immediately after mixing completely decay in 72 h, even decay rate decreased by the additive. Release rate of Ca^{2+} was still slow for all additives except for to rapid for $CaCl_2$, so anti-decay property could not improve effectively. Contrarily, Ca^{2+} ion release from $CaCl_2$ was too fast to form gel network not to allow injection. Low-decay type of the injectable HAp/Col could be prepared by control optimal release rate of Ca^{2+} ion by combination of acid and Ca compounds.

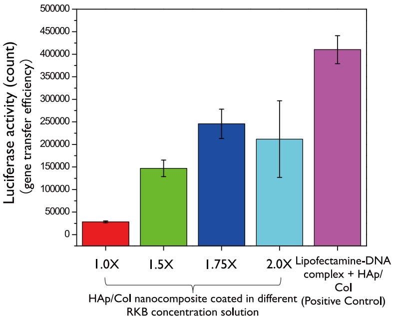

Fig. 2. Transfection efficiency by luciferase activity after 3 days culture of CHO cells on the materials.

(2) Calcium Phosphate Coated Hydroxyapatite/Collagen Nanocomposite for Surface-Mediated Gene Transfer.[2)]

Calcium phosphate (CaP) coating with plasmid DNA (DNA-CaP coating) is a promising candidate for safer and area specific transfection. The HAp/Col is one of the best candidate for large bone repair having osteoclastic resorbable property. To improve transfection efficacy of DNA-CaP coating as well as to improve osteogenic function of osteoblasts on the HAp/Col, luciferase plasmid DNA-CaP coating was formed on a HAp/Col and transfection efficacy was investigated by using luciferase activity of the cell cultured on the DNA-CaP coated HAp/Col. The DNA-CaP coatings were prepared on the HAp/Col by immersing it in luciferase plasmid DNA containing supersaturaterd CaP solutions (Ringer's-Klinisalz-MEYRON (RKM) solutions) with the varied Ca and P concentration levels. Amount of coating layer was increased with increasing in Ca and P concentration of the RKM solution. Amount of DNA immobilized in the CaP layer was increased with Ca and P concentration but satulated at 1.75x level. Transfection efficacy was the same trend as the DNA amount immobilized as shown in Fig. 2. In fact, this efficacy is 4 times higher than conventional CaP-fibronectin system. The results suggested that the HAp/Col coated with DNA-CaP expected to be a safer transfection system as well as a materials for rapid repair of large bone defect.

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Materials for Functional Nanomedicine

Group Leader **Hisatoshi KOBAYASHI**
(Nano-Life Field)

1. Outline of Research

In general, organism selected quite limited molecules such as amino acids, lipids, sugar moieties, and limited metals and inorganics, and combined the limited molecules and finally constructed such highly functionalized complex systems. From the structure point of view, the organism is constructed by various nano-fibers and nano-particles under the highly dimensionally controlled condition.

We are challenging functionalization of a medical device using various nanomaterials and nanotechnologies till now. For example, in order to construct highly biofunctionalized cell-ECM composite, we are aiming to develop nano-micro-macro structure-regulated biofunctional materials which inspired natural ECM. Because it is the way in which organism selected under the evolution.

Towards the clinical use, we are carefully studying the cell-biomaterials interaction from the view point of material science under the world wide collaboration with various medical engineering, medical institutes etc.

2. Research Activities

(1) Detection of p53 gene point mutation using sequence-specific molecularly imprinted PoPD electrode.[1)]

An amperometric sequence-specific molecularly imprinted single-stranded oligodeoxyribonucleotide (ss-ODN) biosensor was fabricated and characterized in this study (Fig. 1). Using ss-ODN as the template and *o*-phenylenediamine as the functional monomer, the ODN biosensor was fabricated by an electropolymerization process on an indium-tin oxide (ITO) coated glass substrate. The template ss-ODN was washed out of the ss-ODN/poly(*o*-phenylenediamine)(PoPD)/ITO electrode using sterilized basic ethanol-water.

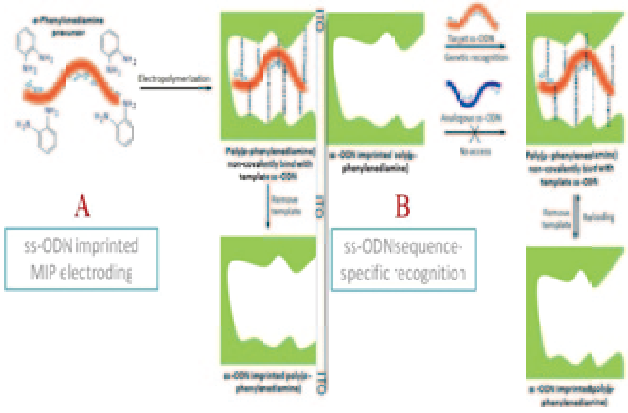

Fig. 1. (A) Electrochemical preparation of ss-ODN imprinted MIP electrode and (B) re-usable biosensor to recognise sequence-specific ss-ODN.

The resulting ss-ODN imprinted PoPD/ITO electrode was characterized (Fig. 2) using Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and cyclic voltammetry (CV). The amperometric responses, i.e., Δ*i* as a function of the target ss-ODN concentration was studied. The biosensor using ss-ODN imprinted PoPD/ITO as the working electrode showed a linear Δ current response to the target ss-ODN concentration within the range of 0.01–300 fM. The biosensor showed a sensitivity of 0.62 μA/fM, with a response time of 14 s. The present novel molecularly imprinted ss-ODN biosensor could greatly benefit in terms of cost-effectiveness, storage stability, ultra sensitivity and selectivity together with the potential for improved commercial genetic sensors.

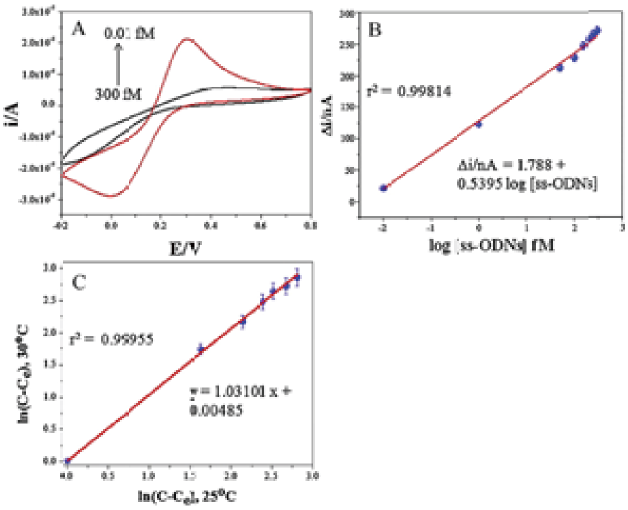

Fig. 2. (A) The cyclic voltammogram of the MIP/ITO electrode in the presence of target ss-ODN, (B) the steady-state _ current response of the MIP/ITO biosensor as a function of the logarithm of molar concentration of the target ss-ODN, and (C) the relative adsorption of the target ss-ODN onto the MIP/ITO electrode at a concentration ranging from 0.01 to 300 fM at 25 and 30 °C. Values of (B) and (C) are mean±SE; %SD = 4.61; n = 5. Working conditions: supporting electrolyte – 10 mM PBS of pH 7.4 containing 1.0 mM Fe(CN) $6^{3-/4-}$ and 0.1 mM KCl at 50 mVs^{-1} scan rate vs. Ag/AgCl.

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Functionalization of Atomic Network Materials

Group Leader **Takao MORI**
(Nano-Materials Field)

1. Outline of Research

Approximately two thirds of all primary energy (fossil fuels, etc) being consumed in the world, sadly turns out to be unutilized, with much of the waste being in the form of heat. The useful and direct energy conversion of waste heat to electricity is a large incentive to find viable thermoelectric materials. Traditionally, high performance thermoelectric materials have tended to not be element friendly; being composed of Bi, Te, Pb, etc. One need exists to develop effective thermoelectric materials composed of abundant and safe elements. Another need exists for materials to have good thermal stability when considering mid to high temperature applications. To this end, we aim to functionalize covalent materials composed of elements like XIII~XV group elements (C, B, Si, Al, Sn, etc) by utilizing their atomic network structure, i.e. clusters, 2D atomic nets, cage-like structures in which the structural order plays a large role in the physical properties.1-3)

2. Research Activities

(1) Control of TE properties by network host atom control.

A series of homologous RE-B-C(N) compounds; $REB_{17}CN$, $REB_{22}C_2N$, and $REB_{28.5}C_4$, was recently discovered to be the long awaited n-type counterpart to boron carbide. Boron carbide is one of the few TE materials which have been commercialized, however, the lack of a compatible n-type counterpart has been a long standing obstacle, with great effort over 20 years being made to find one.

A large advantage of atomic network materials is the tuning of the properties through exchange of the network host atoms. This was previously realized for example in the superior TE properties of boron carbide through B/C control. B/C modification was also tried for $YB_{22}C_2N$. Although the homogeneity region was revealed to be much smaller than boron carbide, C increase in the C-B-C chain was found to improve the properties.4)

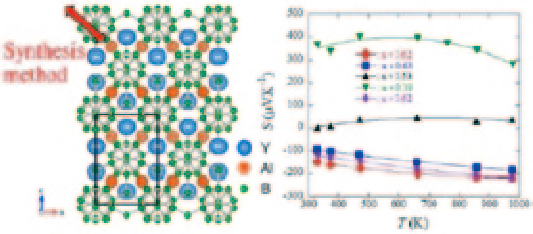

Fig. 1. Excellent pn control of aluminoborides.

(2) Control of TE properties by network encapsulated atom control.

Transition metal doping of the voids in the boron cluster network was found to improve the TE properties of the boron carbide n-type counterparts. Co and V doping of $YB_{22}C_2N$ appear to be the most promising, with the absolute values of the Seebeck coefficient increasing by up to 140%, with a simultaneous significant reduction up to two orders in electrical resistivity. A striking annealing effect was found which showed a further increase of the Seebeck coefficient up to 180%.5,6)

Through particular synthesis processes, we have been successful in synthesizing yttrium aluminoboride, $YAlB_{14}$, with different content of the encapsulated alumunium atom. As a result (Fig. 1), excellent control of p-n characteristics (400 μVK^{-1} to -200 μVK^{-1}) were achieved in a system with the same crystal structure and consisting of the same elements.7)

(3) Other materials.

Very few reports have been made on boron sulfides. We synthesized B_6S_{1-x} from the elements in a Ga melt. Rietveld analysis displayed an α-rhombohedral boron framework of B_{12} icosahedra and a narrow filling fraction range for sulfur atoms in the interstitial voids (0.37 < x 6 0.40). The samples exhibited large Seebeck coefficients, reaching a maximum of 220 VK^{-1}, but a densification process needs to be developed. 8)

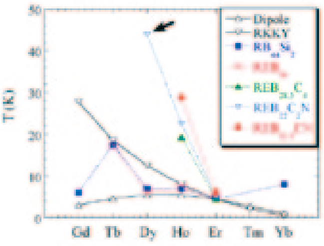

Fig. 2. Magnetism of higher borides.

(4) Developing magnetic properties.

Unexpectedly strong magnetic coupling has been observed in boride insulators containing the B_{12} icosahedra as a structural unit. We had previously successfully synthesized $DyB_{22}C_2N$ which was thought to not be possible because of the relatively large size of dysprosium. Spin glass-like behaviour was observed with a broad peak around 44 K, and this system is indicated to have the strongest magnetic coupling ever observed for any rare earth boride insulator. Conventional mechanisms for f-electron magnetism cannot explain the strong coupling observed (Fig. 2), which further indicates the B_{12} icosahedra as a novel mediator of magnetic interaction. 9)

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Focusing the Light in Nanospace

Group Leader **Tadaaki NAGAO**
(Nano-System Field)

1. Outline of Research

The technology for amplifying, confining, and scattering the light in nanoscale is strongly desired as a key technology in communication, optical sensing, and energy harvesting. 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.[1-2] Atom-scale size effects become pronounced especially in metallic objects, since the Fermi wavelengths of metals are in the Ångström range.[1-2] 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 energy harvesting devices.[2-5]

2. Research Activities

We focused ourselves to the fabrication of various nanoscale optical antennas in visible to infrared spectral region by using both lithographic and self assembly techniques.[1-5] The electromagnetic waves in visible to mid-infrared region can be confined in nanometer-scale and even down to the subnanometer scale structures.

Fig. 1 shows an example of an optical antenna with resonance frequency in the visible spectral region. The highest electric field enhancement is realized in the near field of this bowtie antenna at the narrow gap, and it goes up as high as 90 times of that of the incident light. It exhibited single-peaked antenna resonance and its resonance frequency was found to be tuneable by lifting up the antennas from the substrate surface. The light-focusing/scattering properties of this nanostructure can be utilised in fluorescence microscopy, field-enhanced vibrational spectroscopies for bio-sensing applications, and also in photocatalysis.

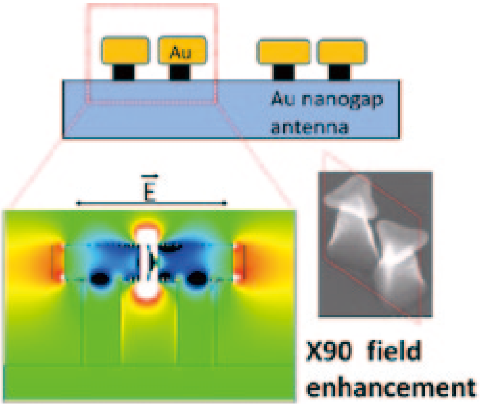

Fig. 1. A cross-sectional view of the Au nanoantenna with resonance frequency in the visible region (top). The electric field enhancement reaches 90 times of the incident light intensity at the nanogap between the two Au nanodots (bottom left). An SEM image of the fabricated nanostructure (bottom right).

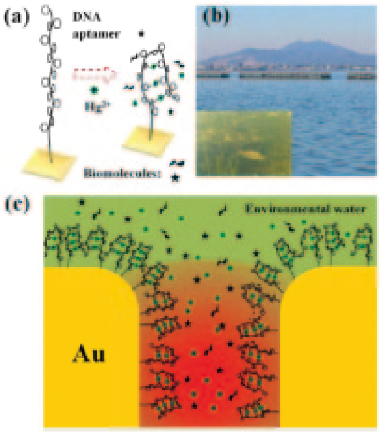

Fig. 2. (a) Schematic of the mercury trapping by a DNA aptamer. (b) A photo of Lake Kasumigaura and subaqueous environment. (c) Structural change in these DNA owing to the adsorption of Hg^{2+} ions that leads to the modification in the optical spectrum, which later leads to the in situ detection of mercury ions in water.

We also demonstrated "part per trillion - ppt" level single-step selective monitoring of mercury ions (Hg^{2+}) in environmental water by plasmon-enhanced vibrational spectroscopy. We combined a nanogap-optimized mid-infrared plasmonic structure with mercury-binding DNA aptamers to monitor *in situ* the spectral evolution of the vibrational signal of the DNA induced by the mercury binding (Fig. 2). The mercury-associated distinct signal is selectively picked up from the background signals including bio-molecule associated signals from lake water and is selectively characterized. For example, with natural water from Lake Kasumigaura (Ibaraki Prefecture, Japan), direct detection of Hg^{2+} with a concentration as low as 37 ppt (37×10^{-10} %) was readily demonstrated. This indicates the high potential of this simple method for environmental and chemical sensing of metallic and ionic species in aqueous solution.

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Characterization of Semiconductor Nanostructures by Using EBIC and CL Techniques

Group Leader **Takashi SEKIGUCHI**
(Nano-Materials Field)

1. Outline of Research

We are now pursuing 4 projects for semiconductors named “Square Si”, “Multi-dimensional EBIC”, “Anything CL”, and “100V EM”. “Defect Control” is the key issue for these projects. Thus, we should characterize various properties of defects in nanoscale. For this purpose, we have developed special electron beam characterization techniques, such as electron-beam -induced current (EBIC) and cathodoluminescence (CL) as well as the secondary electron (SE) imaging. First, we have improved the spatial resolution of EBIC/CL by introducing a better electro-optics and optimizing the light collection system. Second, the new specimen preparation techniques, such as cross sectional polisher (CP) and focus ion beam (FIB) have been introduced.

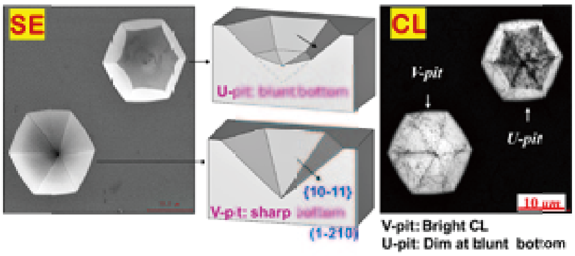

Fig. 1. Planar SE and CL images of V- and U-pits in GaN.

2. Research Activities

(1) CL study of V- and U- pits in GaN (Anything CL).

Free standing (FS-) GaN wafers are expected as the substrates for high power laser diodes due to the high electrical conductivity and strain free nature. Although hydride vapour phase epitaxy (HVPE) is widely used for this purpose, the HVPE GaN wafers are still far from the ideal ones according to V- and U- pits. These pit type defects hinder the creation of a flat mirror surface of FS-GaN wafers. We studied the nature and origin of these defects. Fig. 1 shows the planar SE and CL images of V- and U-pits in a GaN thick film grown on a sapphire substrate. Fig. 2 shows the cross-sectional CL image of this film. This CL image clearly indicates that V-pits with {10-11} facets are created and they are growing larger according to the film growth. Then, their bottom is filled by {10-12} facets and they alter into U-pits. At last, U-pits are filled and buried into the film. Such behavior has been explained in terms of the growth speed difference of facets. It is concluded that the control of the growth condition is important to suppress such defects.[1]

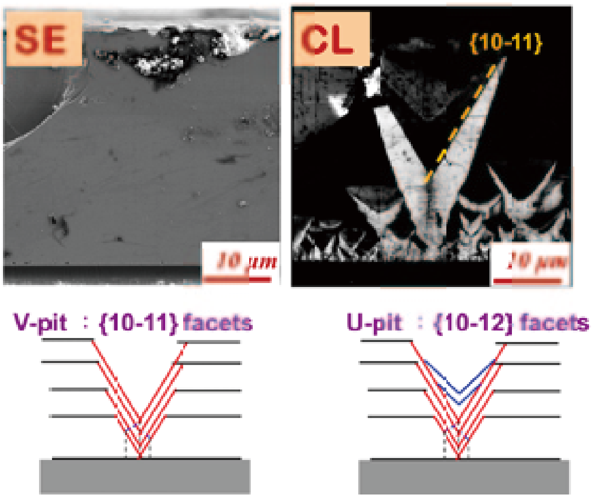

Fig. 2. Cross-sectional SE and CL images of V- and U-pits in GaN.

(2) Characterization of small angle grain boundaries in multicrystalline Si (Square-Si).

Grain boundaries (GBs) in multicrystalline (mc-) Si are regarded as the detrimental defects for solar cell application. However, recent studies have revealed that not all but some special GBs are electrically active. We clarified them by using EBIC/CL and TEM (Fig. 3) and found that Small-Angle (SA-) GBs are more harmful than Large- Angle (LA-) GBs. SA-GBs are imaged as the ensemble of dislocations and categorized two groups, “general” and “special”. The spacing of dislocations is inversely proportional to the misorientation angle. It is found that the general SA-GBs are mainly composed of 60º dislocations, while special ones of edge type dislocations or the mixture of edge and 60º dislocations. The strong electrical activity of special SA-GBs may be attributed to the edge component of dislocations, which is in agreement with the results of glide dislocations introduced into Si crystals by plastic deformation.[2]

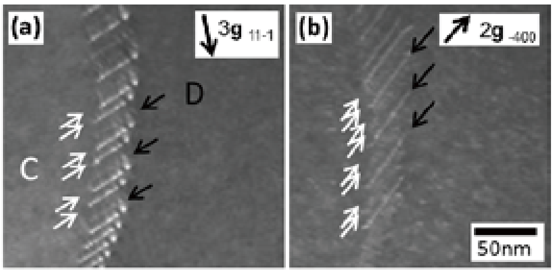

Fig. 3. Weak beam images of general SA-GB. (SA2º).

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Development of Sensor Cells for Nanomaterials Safety Evaluation

Group Leader **Akiyoshi TANIGUCHI**
(Nano-Life Field)

1. Outline of Research

Live cell-based sensors are well accepted and used for investigating various signaling cascades caused by cytotoxic effects of reagents, because of their high specificity and sensitivity to their targets' specific gene expression.1-2) In our laboratory, next-generation sensor cells are fabricated by molecular biology techniques that can detect changes in gene expression in response to toxic substances or other external stimuli (Figs. 1 and 2). We attempted to investigate the interaction between nanoparticles (NPs) and cells through our sensor cells, which can detect stimulation caused by TiO_2 NPs through monitoring induce innate immune responses and other innate cellular stress responses, which we designate as the "First Host Defense System" (FHDS).

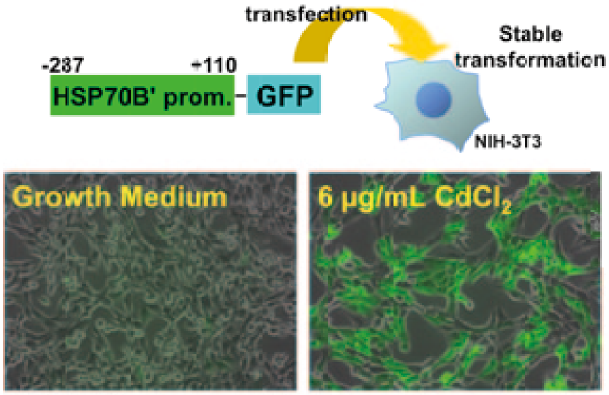

Fig. 1. **Constraction of sensor cells. Sensor cells were constructed by transfecting plasmids that contain promoter and reporter genes such as HSP70B' and GFP genes in to animal cells.**

2. Research Activities

Nanomaterials, expressly nanoparticles, have been manufactured for varied applications. Although they posed a safety risk to our health and environment, recent data have shown the worries concerning their potential toxicity. As we want to develop an effect detection method, how do the nanomaterials affect the cells is important to know. Considering nanomaterials have to be widely synthesized and used for only recent decades, our hypothesis is that there is no enough time for cells to build up specific receptors or signalings for nanomaterials, so the innate cellular defense responses which are against toxins, bacteria, fungi, viruses, and et al., would be used to against the nanomaterials exposure, which we called FHDS. And this FHDS mainly includes inflammatory response, stress response, and genotoxic response. So that, three effective sensor cells have been developed, as following: NF-κB sensor cells, which could detect the inflammatory response; HSP70B' sensor cells, which could detect the stress response; BTG2 sensor cells, which could detect the genotoxic response (Fig. 3) and our work could offer some useful information for the interaction investigation between the nanomaterials and cells.3-6) Moreover, cooperated with different kinds of devices, our sensor cells would be hopeful to be applied for a bio-nanomaterials safety evaluation in the future.

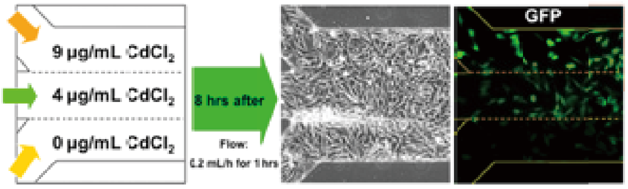

Fig. 2. **Cytotoxic response of the sensor cell line in the 3-inlet microfluidic channels.**

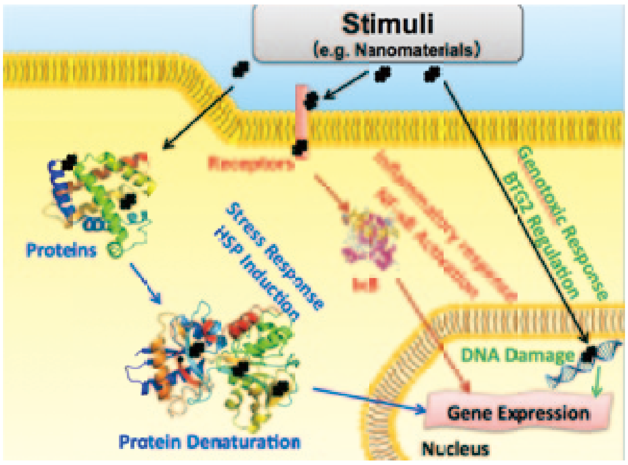

Fig. 3. **"First Host Defense System" mainly includes inflammatory response, stress response, and genotoxic response. So that, three effective sensor cells have been developed, recognized by those receptors, and also a "First Host Defense System" response could be induced by the receptors combined with nanomaterials.**

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Nano-System Computational Science

Group Leader **Yoshitaka TATEYAMA**
(Nano-Power Field)

1. Outline of Research

We are challenging to make novel theoretical frameworks for physicochemical phenomena such as electron transfer, proton transfer & photoexcitation (Fig. 1), since their quantitative calculations are still 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”, and (2) understanding microscopic mechanisms of elementary reactions in physical chemistry problems by applying these computational techniques. Of particular interest are surface/interface electrochemistry in photocatalysis, dye-sensitized solar cell (DSSC), and Li-ion battery.

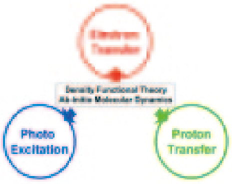

Fig. 1. Research targets in the Nano-System Computational Science group in MANA.

2. Research Activities

(1) Black Dye (Ru N749 Dye) adsorption state on TiO_2 anatase (101) surface. [1,2]

We have investigated the adsorption stability of black dye (Ru N749 dye) on the TiO_2 anatase (101) surface. Geometry optimization and UV spectrum calculation were carried out. Hydrogen bonding between the proton retained in black dye and the surface oxygen is responsible for the stability of the protonated anchor (Fig. 2). We confirmed that the calculated UV spectrum of the most stable dye structure shows the best consistency with the experimental data. This novel aspect of adsorption via protonated carboxyl anchor gives a new perspective for interfacial electronic processes of DSCs. Related to these results, we have also investigated the additive interaction to the black dye, and found that the various binding positions and their effects on the efficiency, which gives a physical implication on the geometry-efficiency relationship.

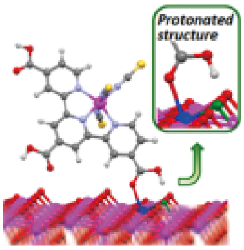

Fig. 2. Calculated stable adsorption structure of black dye (Ru N749 dye) on TiO_2 anatase (101) surface.

(2) Acetonitrile adsorption to TiO_2 anatase (101) surface. [3]

We have also examined the adsorption structures of acetonitrile molecule to the TiO_2 surface with hybrid functional to check the functional dependence of the geometry. Calculations with the HSE06 functional suggest that the pure GGA functional that we have used so far gives reasonable interfacial geometry (Fig. 3).

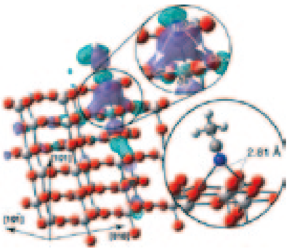

Fig. 3. Calculated adsorption structure of acetonitrile molecule to the TiO_2 anatese (101) interface.

(3) Proposal of a simple method to calculate redox potentials of the DSSC mediators in the acetonitrile solution. [4]

We have proposed a simple method to calculate the redox potentials of the redox mediators in DSSC (Fig. 4), which govern the open circuit voltage related to the efficiency. We have demonstrated that our method can give reasonable estimation for Co complexes, novel mediators, as well as the conventional iodide mediators involving bond cleavage/formation.

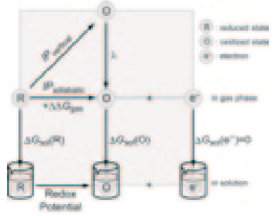

Fig. 4. Scheme of redox potential calculation using the DFT-PCM method with thermodynamics cycle technique.

(4) Structural and electronic properties of CeO_2-ZrO_2 interfaces for charge transfer in SOFC. [5]

Using DFT+U method, we have investigated the vacancy formation and migration energies around CeO_2-ZrO_2 interfaces, focusing on the interfacial strain effects. Our calculations suggested a probable vacancy diffusion path for fast charge transport observed in the experiments.

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On-Demand Nano-Ionics Device with a Range of Electrical and Neuromorphic Multifunctions

Group Leader **Kazuya TERABE**
(Nano-System Field)
MANA Research Associate Rui Yang

1. Outline of Research

The scale of the fine processing for the conventional semiconductor device will reach the atomic scale in near future. It is evident that not only the limits to conventional fine processing technology but also the physical operating limits of semiconductor devices are being reached. One possible way to overcome these technological and physical limits of the existing conventional semiconductor device is to achieve breakthroughs in nanotechnology materials and device-operation principle with increasingly capable. A promising type of the nano-device is the nano-ionics device with multiple functions, which is operated by controlling local ion migration and electrochemical reaction phenomena.

Unique properties and functions, such as analogue memory property, programming rectification, quantized conductance atomic switching, and nonvolatile resistance switching, have been founded in nano-ionics devices[1-3] These properties and functions are realized by the control of local ion migration in a nanoscale electrolyte layer of electronic-ionic mixed conductors or pure ionic conductors.[4] Both cations and anions can be used as the migration ion. In a nano-ionics device functioning as an atomic switch, bipolar resistance switching (BRS), is achieved through the formation and annihilation of a metallic atom bridge by controlling the cation migration in the electrolyte or a nano-gap situated between two electrodes. The cations are usually supplied from chemically active electrodes. Meanwhile, in the transition-metal oxides based nano-ionics device with chemically non-active electrodes, the resistance switching is achieved by controlling the migration of anions, typically oxygen ions.

In this study, we examined the control of the local oxygen ion migration in the tungsten oxide WO_{3-x}, and demonstrate that the WO_{3-x}-based nano-ionics devices perform the unique electrical and brain-type multiple functions, and these functions is configurable on-demand by the control of oxide ion migration and electrochemical reaction.

2. Research Activities

Thin WO_{3-x} films with thickness of approximately 60 nm were fabricated by radio frequency sputtering on Pt bottom electrodes with quartz glass substrates at room temperature.[4] The depositions were performed with a WO_3 targets in a gas mixture containing 80% Ar and 20% O_2. The WO_{3-x} layer was then annealed in situ at 300 °C in an oxidizing atmosphere containing 50% Ar and 50% O_2 at a pressure of 2.67 Pa. Both the Pt top and bottom electrodes were 100 nm thick and were deposited using a metal mask. The dc I–V curves were measured using a four-probe system equipped with a semiconductor characterization system.

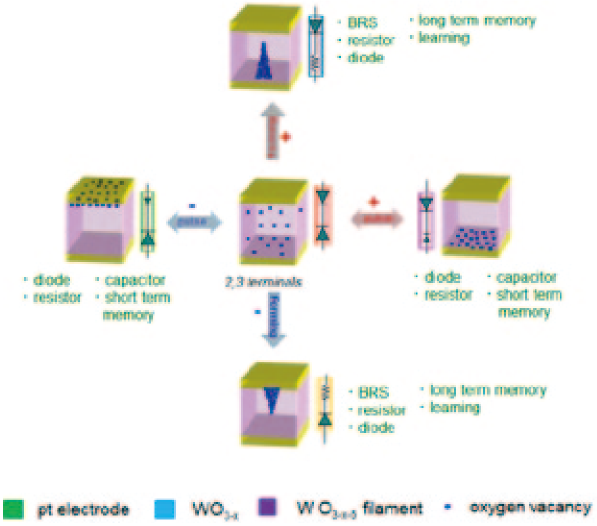

Fig. 1. Schematic depiction of the WO_{3-x} based nano-ionics device with a range of neuromorphic and electrical multifunctions multiple functions which is configurable according to a user demand.

We propose an on-demand WO_{3-x}-based nano-ionics device (Fig. 1), where electrical and neuromorphic multifunction is realized through externally induced local migration of oxide ions and electrochemical reaction.[5-6] The device is found to possess a wide range of time scales of memorization, bipolar resistance switching (BRS), and rectification varying from volatile to permanent in a single device and these can furthermore be realizable in both two- or three-terminal systems. The gradually changing volatile and nonvolatile resistance states are demonstrated to mimic the human brain's forgetting process for short-term memory and long-term memory. The multiple functions are configurable according to a user demand. As shown in the figure, the function of single device can be changed to BRS, diode, capacitor, brain-type memory and so on just by applying voltage to control of oxide ion and electrochemical reaction. We suggest that the nano-ionics device with its on-demand electrical and neuromorphic multifunction has a unique paradigm shifting potential for the fabrication of configurable circuits, brain-type memories, digital-neural fused networks, and more beyond in one device architecture.

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Controlling Initial Cytocompatibility of Bioabsorbable Mg Alloys

Group Leader **Akiko YAMAMOTO**
(Nano-Life Field)

1. Outline of Research

Magnesium and its alloys are expected as bioabsorbable metals in the biomedical field since they are easily corroded by reacting with water in the body fluid. However, excess generation of OH^- by corrosion reaction increases pH of the fluid around Mg surface, which inhibits cell growth on its surface. Therefore, retardation or control of Mg corrosion is a key for the success of bioabsorbable Mg devices.

High Al-content Mg alloys, such as AZ91, is widely applied to industrial uses since they have higher corrosion resistance than Al-free Mg alloys and pure Mg. However, high Al-content Mg alloys suppress cell growth on their surface.1) This may not be attributed to the pH increase by OH^- generation but to the surface properties of high-Al content Mg alloys. It is well known that material surface properties influence cellular function via protein adsorption onto material surface. In this study, surface modification is applied to AZ91 alloy to change its surface property and to improve its cytocompatibility. Silanization is employed to control surface hydrophobicity of AZ91 without changing its degradation behavior. 2)

2. Research Activities

Five kinds of silanes were employed to modify cast AZ91 surface: ethyltriethoxysilane (S1), 3-aminopropyltriethoxysilane (S2), 3-isocyanatopropyltriethoxysilane (S3), phenyltriethoxysilane (S4), and octadecyltriethoxysilane (S5).

X-ray photoelectron spectroscopy (XPS) analysis of unmodified and silanized samples confirmed the existence of silanized layer at the sample surface, which is about 1-1.5nm in thickness for S1. The water contact angle of unmodified and silanized samples were measured as follows; 30° for unmodified, 72° for S1, 57° for S2, 54° for S3, 71° for S4 and 88° for S5.

Albumin is major protein of human blood plasma and employed to demonstrate the effect of silanization on protein adsorption behavior. Albumin adsorption onto unmodified and silanized samples from PBS(-) soln. was shown in Fig. 1. Albumin adsorption increased by silanization depending on the kind of silanes used. The adsorbed amounts of Albumin on S1, S2, and S3 were higher than those on S4 and S5.

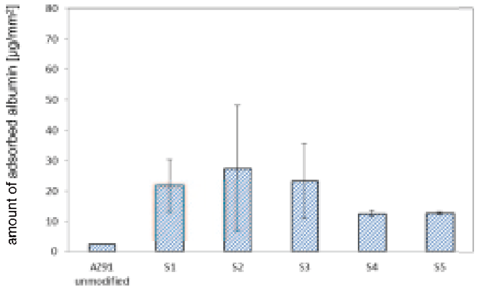

Fig. 1. Amount of adsorbed albumin on unmodified and silanized AZ91 samples.

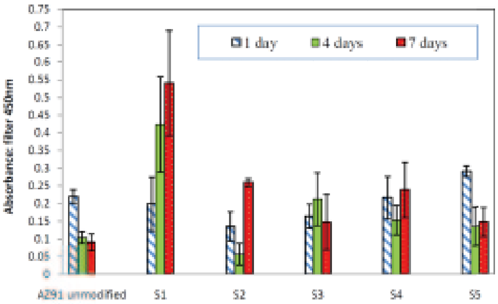

Fig. 2. Proliferation of SaOS-2 on unmodified and silanized AZ91 samples.

Human osteosarcoma SaOS-2 was cultured on unmodified and silanized samples for 1, 4, and 7d. As shown in Fig. 2, there were no significant difference among samples after 1 day of incubation, however, cells on S4 and S5 spread rather than those on S1, S2, and S3. At day 4 and day 7, cells on S1 proliferated well whereas cell growth on other samples was suppressed. Mg^{2+} release was observed for all samples even after 1 day of cell culture and increased along the incubation time. S4 and S5 showed slightly lower Mg^{2+} release ad day 1, but no significant difference was observed among the samples.

Silanization is an effective method to immobilize organic molecules onto metal surface for controlling chemical structure of material surface. Silanization performed in this study increased surface hydrophobicity and changed protein adsorption behavior. S4 and S5, which has relatively high water contact angle, showed relatively low albumin adsorption and more elongated cells at day 1. This fact suggests moderate correlation between surface hydrophobicity and protein adsorption or cell morphology at day 1. However, at day 7, cell growth was only observed for S1. It may be attributed to the small molecular size of S1, which contributes higher density of immobilized molecules and their stability, but further investigation is required to clarify this point.

The results obtained in this study indicated that a very thin layer of ethyl moieties prepared on AZ91 surface is effective to improve initial cytocompatibility without influencing its degradation behavior.

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Nanosheet Electronics

Associate Principal Investigator Minoru OSADA
(Nano-Materials Field)

1. Outline of Research

Two-dimensional (2D) nanosheets, which possess atomic or molecular thickness and infinite planar lengths, have been emerging as important new materials due to their unique properties. In particular, the recent development of methods for manipulating graphene has provided new possibilities and applications for 2D material systems; many amazing functionalities such as high electron mobility and quantum Hall effects have been discovered. This breakthrough has opened up the possibility of isolating and exploring the fascinating properties of 2D nanosheets of other layered materials, which upon reduction to single/few atomic layers, will offer functional flexibility, new properties and novel applications. We are working on the creation of new oxide nanosheets and the exploration of their novel functionalities in electronic applications.

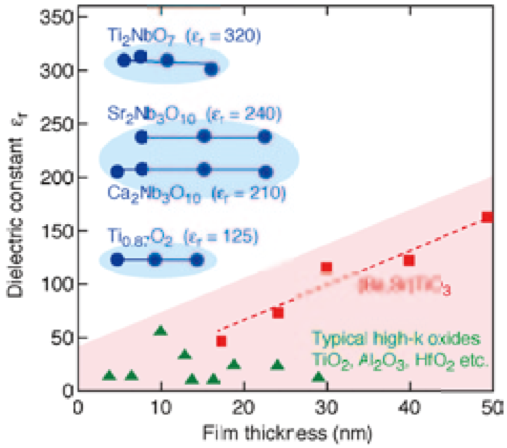

Fig. 2. Maximum values of ε_r for high-κ nanosheets and various oxide thin films.

2. Research Activities

Oxide nanosheets have distinct differences and advantages compared with graphene because of their potential to be used as insulators, semiconductors and even conductors, depending on their chemical composition and structures. There is enormous interest in building devices and functional materials based on 2D oxide nanosheets of different compositions to complement those from graphene. One of the important targets is the development of high-κ dielectric nanosheet, which is a promising potential component for many devices such as memories, capacitors and gate dielectrics.[1] Seeking to develop a new high-κ oxide material, we focus on titania- or perovskite-based nanosheets ($Ti_{0.87}O_2$, Ti_2NbO_7, $LaNb_2O_7$, $Ca_{2-x}Sr_xNb_3O_{10}$) since these nanosheets consist only of key building blocks of highly polarizable TiO_6/NbO_6 octahedra, which make an ideal base for high-κ dielectrics. We delaminated layered oxides and stacked nanosheets on an atomically flat $SrRuO_3$ substrate, creating films between 5 and 15 nm thick (Fig. 1a). The thin films developed by this method have excellent dielectric characteristics, achieving the world's highest performance permittivity (100 – 320) with the thickness down to 10 nm (Fig. 2).[1,2] These nanosheet-based capacitors exceed textbook limits, opening a route to new capacitor devices.

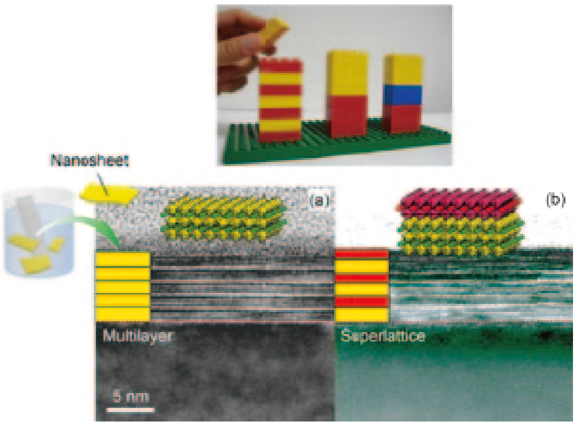

Fig. 1. LEGO-like game using oxide nanosheets. (a) $(Ca_2Nb_3O_{10})_5$ multilayer film. (b) $(LaNb_2O_7/Ca_2Nb_3O_{10})_3$ superlattice.

One more interesting concept using oxide nanosheets is the layer-by-layer engineering of thin-film device architectures. Combining different nanosheets into desired superlattice structures can produce new electronic states at the interface and the opportunity to create artificial materials with novel properties.[3,4] In designing nanostructured ferroelectrics, we fabricated an artificial superlattice (Fig. 1b) by alternately stacking of two perovskite nanosheets ($Ca_2Nb_3O_{10}$, $LaNb_2O_7$).[3] By such an artificial structuring, we found that the ($Ca_2Nb_3O_{10}$/$LaNb_2O_7$) superlattice possesses a new form of interface coupling, which gives rise to ferroelectricity at room temperature. This artificial superlattice exhibited robust ferroelectric properties even at several nanometer thicknesses, which is essentially required for future memories.

Our work is a proof-of-concept, showing that high-performance electronic devices can be made from oxide nanosheets. Our new recipe is not suitable for immediate use but it could offer the next big change in our electronics in the coming decades.

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Laser-Based Inelastic Photoemission Spectroscopy

MANA Independent Scientist Ryuichi ARAFUNE

1. Outline of Research

My main objective is to explore and elucidate some aspects of the interaction between light and matter that take place uniquely at the solid surfaces. Currently, we concentrate on developing laser-photoemission spectroscopy (PES) into a novel technique to probe surface dynamics. Vibrational dynamics of adsorbate-substrate modes of adsorbed atoms and molecules can yield direct information on the nature of the bonding with the surface and on the energy exchange between the adsorbate and the substrate. Such modes appear at low-energy region (<100 meV). Unfortunately, no time-resolved surface vibrational technique that is applicable to low-energy vibrational modes has been developed thus far. Thus, a novel technique that can access such low energy vibrational modes is highly demanded.

Recently, we found that the photoemission spectra excited by the laser light contained the vibrationally induced inelastic components.1) This result indicates that the laser-excited and low-energy photoelectron strongly interacts with vibrational elementary excitations. We believe that this inelastic interaction has potentiality for measuring the dynamics of the electron-vibration interaction. The aim of this research project is the development of a novel PES and measurement of the vibrational dynamics (including the charge transport property) at solid surfaces. By measuring low energy photoelectron spectra of surfaces excited by the pulse laser light whose energy is tuned slightly higher than the work function of the solid surface, we will elucidate some aspects of the dynamic interactions between low-energy electrons and surface elementary excitations. This technique enables us to investigate vibrational and electronic dynamics of adsorbate on solid surfaces in the time range of picoseconds to femtoseconds.

2. Research Activities

(1) Very high energy-resolved two-photon photoemission.

Combining narrowband short pulse laser excitation with energy- and angle-resolved two-photon photoemission (2PPE), we have investigated the electronic properties of the Cu(001) surface. A picosecond Ti:Sapphire laser and UHV-system equipped with a 2D-electron detector offer new insight into electron dynamics in a photoexcited states on solid surfaces with the millielectronvolt level, which cannot be achieved with the ultrafast (≤100 fs) laser excitation.

Lifetime of the electrons in the excited states (the intermediate states in the 2PPE process) are governed by Quasi-elastic and inelastic scattering. The former determines the so-called pure dephasing rate Γ^*, the latter the decay rate Γ. The ultrafast time-resolved 2PPE experiments enable us to determine the decay rate. The linewidth of the 2PPE spectra Γ_{tot} is described by $\Gamma_{tot} = \Gamma + 2\Gamma^*$, and Γ is comparable to the line width of the ultrafast laser pulse. Thus, high energy resolved 2PPE exited by the narrow band laser is highly required for accurately determining the pure dephasing rate.

In this year, we have achieved the highest energy resolution (<10 meV) by the narrowband picosecond pulse laser excitation. The image states were well separated in the spectra up to n=4, and the energy positions of the higher image states (n = 5, 6, and 7) were determined. Finally, we have succeeded in measuring the pure dephasing rate for the n = 1 and 2 image states.

(2) Vibrational characterization of CO on metal surfaces.

Adsorption site and vibrational energies of CO on a clean Ag(001) surface were determined using scanning tunneling microscopy, inelastic electron tunneling spectroscopy with a scanning tunneling microscope (STM) and high resolution electron energy loss spectroscopy (HREELS). The CO molecules were found to adsorb on atop site of the Ag(001) surface, which was similar to their adsorption on the Cu(001) surface where CO rather weakly chemisorbs. The vibrational energy of the CO internal stretching mode was found to be 263 meV, which is only 3 meV less than that of CO in the gas phase. In contrast to Cu(001) which is one of the most comprehensively studied system, this result indicates that the CO molecules chemisorb very weakly on the Ag(001) surface. The low energy of vibrational energy of the metal-C stretching mode also manifested very weak chemisorption. In spite of weak chemisorption, we have succeeded in determining the vibrational energy of two frustrated modes with inelastic tunneling spectroscopy with STM. The vibrational energies determined by STM-IETS agree with the data taken by HREELS with the off-specular geometry.

(3) Geometric and electronic structure of silicene on Ag.

Recent theoretical studies have shown that freestanding silicene, which is the counterpart of graphene, is stable and forms buckled structure. Furthermore, fascinating electronic property, such as a Dirac cone, is predicted even in the buckled structure. While freestanding silicene has not been synthesized so far, several groups reported the silicene growth on the solid substrate. On the solid substrate, silicene forms buckled structure. Silicene is more flexible than graphene. The high structural flexibility is expected to be controllability of the lattice constant by tuning growth condition. We have demonstrated that the lattice constant of silicene grown on Ag(111) depends on the growth condition especially the substrate temperature. We found four commensurate phases as silicene on Ag(111), which were 4×4, $\sqrt{13}\times\sqrt{13}R13.9$, $\sqrt{19}\times\sqrt{19}R23.4$ and $4/\sqrt{3}\times 4/\sqrt{3}R30$.We also succeeded in observing STM image corresponding two of these phases, namely 4×4 and $\sqrt{13}\times\sqrt{13}R13.9$, which were consistent with DFT calculations.

Search for New Ferroelectric, Magnetic, and 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 elements.

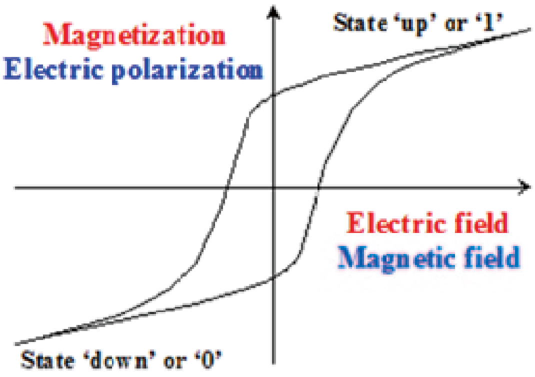

Fig. 1. Ferroelectric/ferromagnetic hysteresis loop: the basis of many memory elements.

2. Research Activities

(1) 'Exotic' perovskites with small ions at the A site.[1)]

'Usual' perovskite-type compounds with the general formula ABO_3, where A is La-Lu and Y and B is V, Cr, Mn, Fe, Co, Ni, and Cu have been attracting a lot of attention for decades. 'Exotic' perovskites are also highly interesting because new phenomena may emerge in them. The term 'exotic' may include compounds with unusual oxidation states, unusual ion distribution, and unusual ions at the A site and B site. Perovskites with A = Sc and In have small tolerance factors, and they can be prepared only at high pressure. We investigated in details properties of $ScCrO_3$ and $InCrO_3$. Some peculiarities were found in comparison with the $ACrO_3$ family. A limited number of other compounds could also be prepared at 6 GPa.

(2) $BiGaO_3$-based perovskites as a large family of polar materials.[2)]

We investigated solid solutions of $BiGa_xM_{1-x}O_3$ (M = Cr, Mn, and Fe) and found the formation of a large family of polar materials with $R3c$ and Cm symmetries. The $R3c$ phases have the same structure as $BiFeO_3$, and the Cm phases have the structure of $PbTi_xZr_{1-x}O_3$ ($x \approx 0.45$). The most surprising feature of the solid solutions of $BiGa_xM_{1-x}O_3$ is the existence of the Cm phase in wide compositional ranges for all compositions. The Cm phase exists in solid solutions of $PbTi_xZr_{1-x}O_3$ at a very narrow compositional range of x = 0.45-0.47 and is believed to be at the origin of excellent piezoelectric properties of this composition. Therefore, thin films of $BiGa_xM_{1-x}O_3$ might be promising lead-free materials to replace $PbTi_xZr_{1-x}O_3$.

(3) Centrosymmetric hexagonal manganite $InMnO_3$.[3)]

Hexagonal manganites $AMnO_3$ are multiferroic materials in which ferroelectricity and antiferromagnetism co-exist. Their fundamental properties have been investigated for half a century. $InMnO_3$ seemed to be similar to other members of the $AMnO_3$ family. However, our previous studies revealed that $InMnO_3$ is not ferroelectric. In the recent study, we combined the first-principle calculations and XRD, SHG, and PFM experimental methods to understand its anomalous behavior. We found that the polar and centrosymmetric structural models are very close in energy in comparison with other members of the family. Our findings have implications for understanding multiferroic properties of $AMnO_3$.

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Optically- and Electrically-Driven Dual-Gate Transistors with Photochromic Channel Layers

MANA Independent Scientist Ryoma HAYAKAWA

1. Outline of Research

Organic electronic devices have considerable attention for realizing printable and flexible logic circuits. In the last decade, great progress has been made as regards the performance of organic field-effect transistors (OFETs).[1] The further development of novel OFETs with specific functionality is attracting attention with a view to providing a new direction for organic electronics.

Among these attempts, we have propose optically- and electrically-driven dual-gate transistor with photochromic channel layers where diarylethene thin films are used as transistor channel (Fig. 1).[2] Diarylethene molecules are well known as represented photochromic molecules. Most essential point is that the photoisomerization induces a large change in the π-conjugation in the molecules. The feature provides considerable change in the conductance. The conductance of closed-ring isomers has been reported to be 1-3 orders of magnitude greater than those of open-ring isomers.[3] We demonstrated for the first time that diarylethene thin films worked as transistor channel. Then, we attained light-induced manipulation of the drain current. The on/off ratio driven by light is 10^2. The value is much larger than those of conventional OFETs. These findings would lead to realizing unique organic devices such as synapse-like organic circuits and human-eye-like sensors.

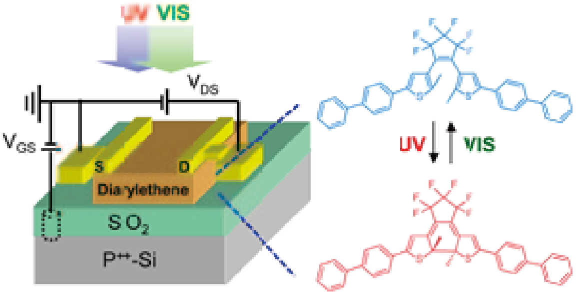

Fig. 1. Schematic illustration of a diarylethene-channel transistor.

2. Research Activities

(1) Transistor properties of diarylethene thin films.

Fig. 2(a) and 2(b) show the drain current (I_d) – drain voltage (V_d) and drain current (I_d) – gate voltage (V_g) characteristics of diarylethene transistors. Before the measurement, the sample was irradiated with UV light for 5 min to elevate the closed-ring to open-ring isomer ratio. The ratio of closed-ring isomers was calculated to be 75%. The results clearly demonstrated that the diarylethene films behaved as a p-type channel transistor. The on/off ratio multiplied by the gate voltage was calculated to be 10^3. The carrier mobility and the threshold voltage were $1.0\pm0.2\times10^{-5}$ cm^2/Vs and -64±10 V, respectively.

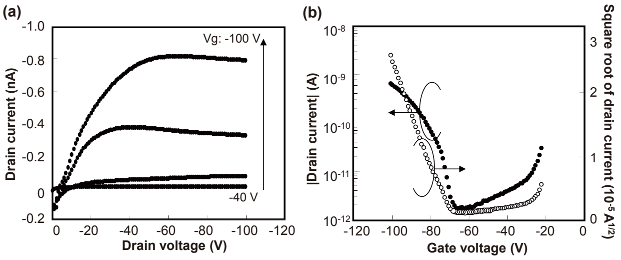

Fig. 2. (a) Drain current-drain voltage and (b) drain current-gate voltage curves in diarylethene transistors.

(2) Optical manipulation of the drain current in diarylethene-channel transistors.

We then examined the light-field effect on the drain current. Light irradiation was found to induce a marked modulation in the drain current as shown in Fig. 3. First, the drain current was completely suppressed after VIS light irradiation for 2 min. UV light irradiation for 3 min then induced a reversible change, and the diarylethene layer again worked as a transistor channel. In this way, a reversible change in the drain current was repeatedly observed by alternating the UV and VIS light irradiation. An on/off ratio of about 10^2 was realized with an optical gate. The value is much larger than seen in other transistors that employ photochromic molecules (10 - 80 %) and comparable to that driven by electrical gate. These results indicate that the drain current was manipulated by two gates, namely, optical and electrical gates. Our findings demonstrate the potential to achieve high-performance opto-electrical organic devices including optical sensors, optical memory and photoswitching transistors.

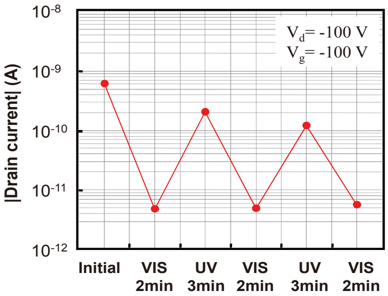

Fig. 3. Optical modulation of the drain current (V_d= -100 V and V_g= -100V) against a sequence of photo-irradiation.

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Composite Materials Systems for Optics and Catalysis

MANA Independent Scientist Joel HENZIE

1. Outline of Research

Nanocrystals are building blocks for a new class of functional, composite materials that can be completely assembled from the bottom up. In these materials, the colloids behave as the ‘atoms’ and ‘molecules’ of large-scale, ordered supercrystals that can exhibit collective physical properties that may not be found in nature or in conventional bulk materials. The main theme of our research is to understand the complex chemical and physical processes that are important in the formation of these unconventional materials. Through this work we will address multiple fundamental and applied research questions ranging from nanocrystal synthesis to bottom-up self-assembly to artificial photosynthesis and heterogenous catalysis.

2. Research Activities

(1) Shape-controlled synthesis of novel nanomaterials.

Understanding the complex interplay between kinetics and thermodynamics is key to developing a general mechanism for describing the control and evolution of nanoparticle shape in colloidal synthesis. Our research methods rely on the development of inexpensive high throughput and combinatorial tools to rapidly explore chemical reaction space. Our goal is to isolate the most important parameters that control colloid shape and monodispersity in a wide variety of materials (Fig. 1).

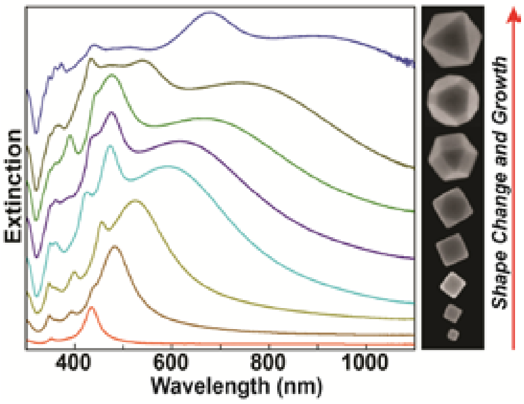

Fig. 1. Absorbance spectra and scanning electron micrographs (SEM) show Silver (Ag) nanoparticles as they simultaneously grow and change shape from cubes to octahedra.[1]

(2) Bottom-up assembly of 3-dimensional plasmonic metamaterials.

Metamaterials are artificial superstructures that have optical properties that may not be found in nature. Typically, plasmonic metamaterials are composed of arrays of sub-wavelength metal and dielectric components that affect and manipulate the propagation of light waves by virtue of their precise shape, arrangement and connectivity. Colloidal nanocrystals are ideal building blocks for metamaterials because they can be synthesized with exquisite control of particle shape, and eventually assembled into complex superstructures.

A major part of our self-assembly efforts focus on how to control the fundamental interparticle interactions and driving forces. This enables us to assemble polyhedral particles over a continuum of sizes---from individual particles to small particle clusters to extended supercrystals.[1] By developing these methods we can show experimentally how the optical properties of metal structures dramatically change as the size and connectivity of the metal superstructure grows and becomes a 3D metamaterial (Fig. 2).

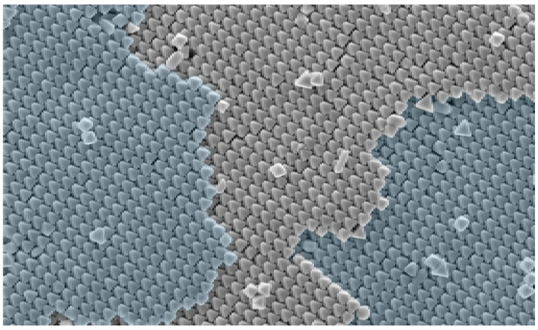

Fig. 2. Colored SEM showing different layers on the surface of a millimeter-scale Minkowski supercrystal composed of nanoscale Ag octahedra.[2]

(3) Artificial Photosynthesis.

Artificial photosynthesis is a promising approach for renewable energy generation and storage because sunlight can drive this chemical reaction to generate hydrogen fuel. Yet the need for new energy harvesting materials is critical because no one material currently satisfies all the physical and chemical criteria necessary to make this method competitive with fossil fuels. The challenge for materials chemists is how to efficiently discover new photocatalysts with the desired properties and accelerate research beyond the slow, iterative process currently employed on the benchtop. Our research uses high-throughput and combinatorial synthesis tools to search for colloidal structures that are good photocatalysts. By employing these massively parallel reaction schemes both for synthesis *and* materials characterization, we can rapidly discover how different colloids and colloidal superstructures improve on existing industrial photocatalysts.

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Development of Fully Printed Organic Electronics Devices of High Performance

MANA Independent Scientist Takeo MINARI

1. Outline of Research

The solubility and low processing temperatures of organic semiconductors enable fabrication of electronic devices using simple printing technologies. In particular, formation of all the layers of organic electronics devices by using printing techniques is essential, because it enables fabrication of devices under ambient atmosphere without use of vacuum processes. Thus, the production cost of semiconductor devices can be substantially reduced by using printed electronics technology.[1)] In this sense, I have developed an all-solution-processed fabrication process of organic field-effect transistor (OFET) arrays, in which all the layers of OFET devices (gate electrode, gate insulator, source/drain electrodes, and organic semiconductor layer) are formed by solution-based patterning techniques under ambient atmosphere.

2. Research Activities

(1) High resolution printing of electrical circuit by using patterned surface wettability.

One of the requirements for fabrication of semiconductor devices by printing is resolution of the printed pattern. In order to form the high resolution pattern by printing, we used surface wettability difference patterned by irradiation of vacuum ultra violet (VUV) through a photo mask (Fig. 1). The selected areas of hydrophobic surface were irradiated with VUV light, and these areas turned into hydrophilic regions. After that, metal nanoparticle ink was applied to the patterned surface. It selectively adhered only to these hydrophilic regions and thus conductive lines of can be obtained with high resolution.

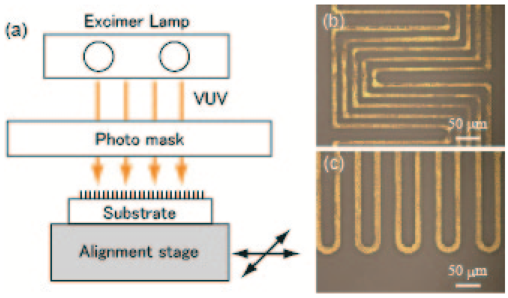

Fig. 1. (a) schematic of the VUV irradiation process. (b), (c) By using surface wettability difference patterned by VUV irradiation, metal nanoparticle ink can be patterned with high resolution.

(2) Fabrication of OFET arrays on a flexible substrate.

By using the high resolution printing technique, we developed fully printed organic field-effect transistor arrays on a plastic substrate. All of the processing was performed below the glass transition temperature of the plastic substrate. Metal nanoparticle ink was used for the source/drain and gate electrode formation, and a soluble organic semiconductor was used for the active layer (Fig. 2). We first carried out source/drain electrodes patterning on the hydrophobic substrate surface. The electrode regions were exposed to VUV irradiation through a photo mask and the exposed surface regions were then made hydrophilic by surface chemical reaction. The metal nanoparticle ink was then applied to the substrate. Thus the source/drain electrodes were formed. On the next step, organic semiconductor layers were patterned between the electrodes by using the same method. Then, the polymer gate insulator was formed on the semiconductor layer by spin coating. Finally, top gate electrode layers were formed to complete fabrication of the OFET devices.

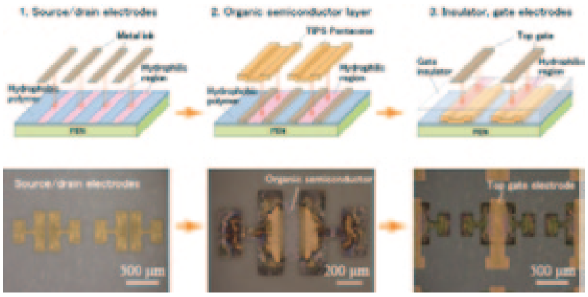

Fig. 2. Fabrication processes of fully printed OFET devices on a plastic substrate.

Using a plastic substrate and a polymer insulator, the result is a fully flexible OFET array. The fully printed OFET array is shown in the optical micrograph in Fig. 3. The total patterning of the electrodes and the semiconductor layers results in complete separation between the devices, which is essential for reducing the gate leakage current and inter-device crosstalk.

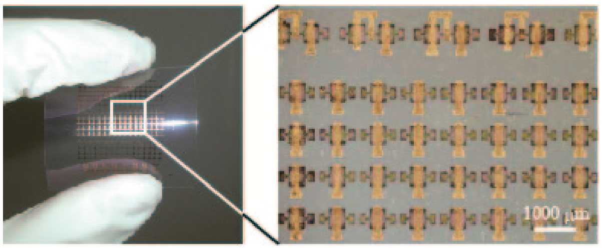

Fig. 3. Fully printed OFET arrays on a flexible substrate.

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Quantum-Dot Devices in Nanostructured Materials

MANA Independent Scientist Satoshi MORIYAMA

1. Outline of Research

A quantum dot is a small metallic island with a single electron charging effect and zero-dimensional confined states, which resembles to the natural atom. For this reason, the quantum dot is often called an artificial atom. Although the atom-like physics is studied their interaction with light, artificial atoms can measure electron transport properties in solid state systems. Therefore, quantum dots are expected for future electric devices that can control the single-electron charge and spin states. Unique features of the quantum dot are the single electron charging effect and the quantized energy levels, and the characteristic energy for the former is the charging energy for an single electron ($E_c = e^2/C_\Sigma$: C_Σ is the self-capacitance of the dot) and is the mean zero-dimensional level spacing (ΔE) for the latter. The single electron devices only need the small dot size for the higher temperature application. The quantum computing devices which may use both the single electron effect and the quantized level need quantum coherence as well. Based on the above background, we explore novel quantum-dot devices that have different functions with conventional transistor. As the working temperature of these devices is directly related to the size of their island, they have motivated the study of transport properties through novel nanostructured materials.

2. Research Activities

(1) Quantum-dot behavior in nanostructured graphene with direct contacts.[1)]

The recent discovery of graphene has opened a door to new vistas of low-dimensional physics. The corresponding energy dispersion becomes the so-called Dirac cone, which leads to rich physics inherited from quantum electrodynamics. In terms of applications, the 2-dimensional sheet structure of graphene and its properties of ballistic transport and high mobility make graphene a promising candidate for future electronic devices. Nanostructures on graphene sheets can be fabricated by carving out of the graphene sheets directly, and the spread 2-dimensional sheet structure may open a door to realize the integrated quantum nano-device system.

In most cases, the formation of graphene quantum-dot devices relies on the removal of unwanted areas of graphene by etching.[2-3)] The performance of such quantum dots is limited due to the detail of nano-constriction structures. Therefore, it is crucially important to develop other methods of creating graphene nanostructures and control the constriction. Here, we propose an alternative device structure for achieving “confinement,” in which nanostructured graphene islands are perfectly isolated and metallic contacts are directly deposited onto them without constrictions. Such a configuration realizes direct contact with a nanostructured two dimensional electron gas (2DEG) system. This device structure may lead to various types of nanojunction 2DEG systems, e.g., superconductor (or magnet)-nano2DEG junction, by selecting the contact materials. Therefore, we believe that this approach may open the door to the development of new graphene-based quantum devices. Transport spectroscopy measurements of this device structure revealed Coulomb blockade behavior at low temperatures, indicating that a multiple quantum dot system is formed in the device. These results are an important step toward increasing our understanding of quantum transport in nanostructured graphene and the realization of single-Dirac fermion devices.

(2) Single-electron transport in ultra-thin Au nanowires.[4)]

Ultra-thin gold nanowires (AuNWs) with uniform diameters of 2 nm and lengths of up to 100 **μ**m are synthesized via the reduction of gold (III) chloride in an oleylamine matrix and they are coating with oleylamine as a surfactant. Therefore, using AuNWs as Coulomb islands, higher charging energy, connection into electrodes and gating effectively can be expected. The fabrication of the single-electron transistor consists mainly in dispersing AuNWs on a doped substrate that serves as a back gate and forming a contact with bottom-contacted source and drain electrodes. On a *p*-doped Si substrate oxidized to form a 400 nm thick SiO_2 top layer, the AuNWs solution is spin-coated and dried under vacuum.

Low temperature transport measurements were carried out at ^{3}He cryostat. The experimental results reveal that the device acts as single-electron transistors in which the electrons though the quantum dots flow one by one. Fig. 1 shows the color scale plot of the differential conductance (dI/dV_{sd}) as a function of source-drain voltage (V_{sd}) and gate voltage (V_g) at 230 mK. Regular Coulomb diamonds such as triangle-shaped were observed.

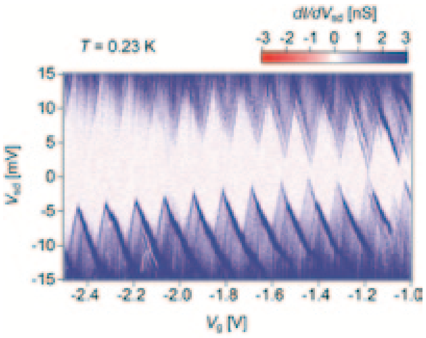

Fig. 1. A color scale plot of the differential conductance (dI/dV_{sd}) as a function of source-drain voltage (V_{sd}) and back gate voltage (V_g), measured at 0.23 K.

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Development of Photoresponsive Biointerfaces

MANA Independent Scientist Jun NAKANISHI

1. Outline of Research

Biointerface is an interface between biomolecules and materials. It plays a pivotal role in biomedical devices such as materials for drug delivery, tissue engineering, and bioanalysis. The major purpose of the present study is to develop chemically functionalized biointerfaces with photochemically active compounds and apply them for analyzing and engineering cellular functions (Fig. 1).

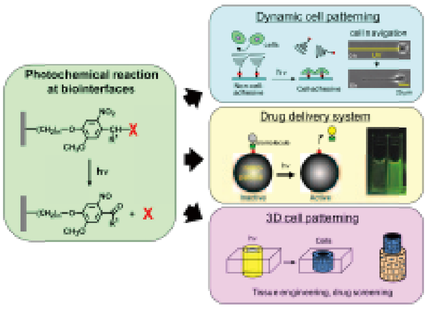

Fig. 1. Photoresponsive biointerfaces developing in this study.

2. Research Activities

(1) Dynamic Substrate Based on Photocleavable Poly (ethylene glycol).[1)]

Dynamic substrates whose cell adhesiveness changes in response to an external stimulus are useful to induce cell migration or array heterotypic cells. The requirements for such applications are high switching efficiency in cell adhesiveness as well as long-term persistence of the created cellular patterns. We prepared a dynamic substrate bearing photocleavable poly(ethylene glycol) (PEG) and examined the effect of the surface PEG density and the charge of cationic base materials on these requirements. An amino-terminated substrate with a certain amino group density and charge was functionalized with photocleavable PEG5K, with and without subsequent backfilling of photocleavable PEG2K. The PEG chains made the surface non-cell-adhesive, but subsequent near-UV irradiation of the substrate induced photocleavage of the PEG, eventually making the surface cell-adhesive. Although the density of amino group in the base material affected both the grafting efficiency of the backfilling PEG and the electrokinetic potential, the latter determined the protein- and cell-repelling abilities of the substrates. Furthermore, varying the surface compositions had almost no effect on the switching efficiency at the early stage of the culture, but it became more significant after culturing cells for a longer time. These results indicate that the zeta potential is an essential factor for long-term persistence of cellular patterns on photoactivatable substrates (Fig. 2). This study not only provide a recipe for the development of a dynamic substrate with an adequate time frame, but also clarifies how the interfacial nanoarchitectures, composed of the nanometer-scale PEG brushes and charged base materials, affect biocompatibility.

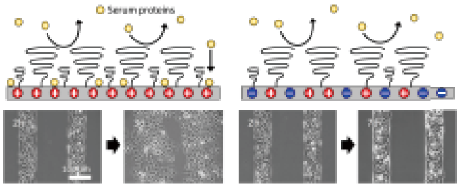

Fig. 2. Zeta Potential Determines Capability of Geometrical Cell Confinement.

(2) Phoactivatable epidermal growth factor based on gold nanoparticles bearing a photocleavable reactive group.[2)]

In this study, a method for the OFF/ON photoswitching of an activity of a protein by using gold nanoparticles (GNPs) bearing photocleavable nitrilotriacetic acid (NTA) among poly(ethylene glycol) (PEG) brushes. An oligohistidine-tagged epidermal growth factor (EGF) was trapped on the GNP surface via a Ni^{2+}-NTA-oligohistidine tertiary complex and released to the bulk solution by near-UV irradiation (Fig. 3). The activity of EGF was suppressed on the sterically-crowded GNP surface, but was retrieved after its photorelease. This method will be useful to develop caged proteins for exploring their spatiotemporal dynamics in inter- and intracellular signal transduction.

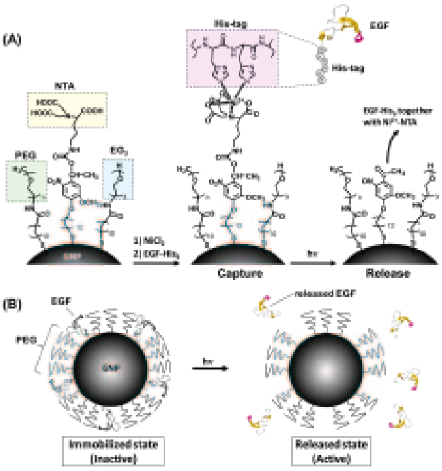

Fig. 3. Photoresponsive GNPs for caging oligohistidine-tagged proteins. (A) Capture and photorelease of EGF-His$_6$ by a GNP bearing disulfides with photocleavable NTA (1), PEG5K (2), and EG3 (3). Disulfide ligands are shown in thiolate forms for clarity. (B) EGF activity change by its photorelease from the nanoparticle.

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Green Nanochemistry: Bandgap Engineering for Group IV Nanostructures

MANA Independent Scientist Naoto SHIRAHATA

1. Outline of Research

Findings of strong luminescence from nanostructures of group IV semiconductors and their compounds, i.e., Si, Ge, Si_xGe_{1-x}, and silicide, have generated a great deal of excitements because their light emitters have a potential to open a new door to silicon photonics. Furthermore, the industrial use of efficiently luminescent group IV nanostructures possibly overcomes the unstable supply issue of rare-earth elements which raises a threat to the present industry of light emitters including LED and laser devices, and would give the significant contribution to realize a lightning industry for sustainable future.

2. Research Activities

(1) Deep-Green Light Emitting Ge Nanocrystals.[1]

This is the first report on germanium nanocrystals (Ge NCs) emitting the light in the "deep-green" wavelength region. Surprisingly, the light emission is highly efficient, and its spectral linewidth is as narrow as 55 nm which satisfies the requirement for the application to LED illumination. The deep-green luminescent Ge NCs have been synthesized by one-step laser ablation process. The NCs are thoroughly characterized by TEM, Raman and optical spectroscopic techniques.

The relationship between the size and the emission is investigated through spectroscopic analyses to reveal the appearance of the quantum confinement effect. Due to strong quantum confinement of photogenerated carriers in diamond cubic Ge NCs and well-controlled size distribution, we successfully fabricated deep-green luminescent Ge NCs with a 17% of absolute PL quantum yield (QY) which was measured using a film form of Ge NCs. The present PL QY is the highest among the values of luminescent Ge NCs reported in elsewhere. Our success of the synthesis of efficiently green-luminescent Ge NCs suggests the possible increase of PL QYs of others such as blue and UV luminescent Ge NCs based on the assumption that those luminescence also appear due to the quantum confinement effect.

(2) Separation of Ge NCs by Emission Color.[2]

The present study reports a new concept to produce Ge NCs with each monochromatic light of fluorescence. There are many papers about size control synthesis of Ge NCs, and what is the common to be said in those papers is that the size of NCs are controlled during the synthesis performed under the severe conditions. In contrast, we challenge to separate NCs from one parent sample by emission color.

It is revealed that rigorous control over size and surface of germanium nanoparticles allows the fine color-tuning of efficient fluorescence emission in the visible region. The spectral line-widths of each emission were very narrow (< 500 meV) than ever before. Furthermore, the absolute fluorescence quantum yields of each emission were estimated to be 4-15% which are high enough to be used as fluorescence labeling tags. In this study, a violet light emitting nanoparticle is demonstrated as a new family of luminescent Ge. Such superior properties of fluorescence were, respectively, observed from the fractions separated from one mother Ge nanoparticle sample by fluorescence color using our developed combinatorial column technique. It is commonly believed that a broad spectral line-width frequently observed from Ge nanoparticle appears due to an indirect bandgap nature inherited even in nanostructures, but the present study argues that such a broad luminescence spectrum is expressed as ensemble of different spectral lines, and can be separated into the fractions emitting the lights in each wavelength region by the appropriate post-synthetic process.

(3) White-Light Emitting Liquefiable Si Nanocrystals.[3]

Due to the serious supply issue of rare-earths, there is a pressing need to develop the potential replacements for them in artificial lightning industory. One of the possible answers is the use of NC quantum dots of compound semiconductors or organic dyes which are in the front line of white light emitting materials. However, efficiently luminescent compound semiconductor NCs contain cadmium, arsenicum and/or lead, possibly leading to the disastrous effect in the spread of the photonics industry because of their toxicities.

We focused on Si as a potentially attractive alternative, and successfully developed white light emitting silicon nanocrystals (Si NCs, Fig. 1), which have been prepared from Si powder through a facile route including HF-HCl etching. Due to broad size distribution, the light emission spectrum covers the whole visible wavelength with a 230 nm of FWHM. Covalent attachment of octyl monolayers to the Si surface changes the physical nature of the NCs from solid into solvent-free liquid, and gives a high thermal stability of the PL feature even under ambient conditions.

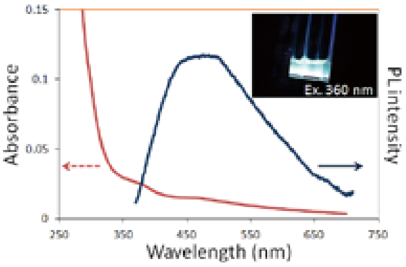

Fig. 1. White-Light Emitting Liquefiable Si Nanocrystals.

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Rational Design of Fuel Cell Electrodes: From Atomic Scale to Micron Scale

MANA Independent Scientist Satoshi TOMINAKA

1. Outline of Research

Fuel cells are one of the important power sources for reducing carbon dioxide emissions. For the successful exploitation of them, stable and low-cost electrode materials having catalyst activity and large specific surface area, and electron conductivity are necessary. Specifically, the electrodes are porous and need three different paths for electrons, ions and fuel molecules, and hence their porous structures are of great importance as well as materials. Here I introduce my recent research works on nanomaterials and technology for arranging porous nanostructures.

2. Research Activities

(1) Nanostructured electron-conductive TiO_x.[1-3]

Reduced titanium oxides are chemically stable and some of them are known to be highly electric conductive, and thus have been expected to be applicable as corrosion-resistant electrodes alternative to precious metals. However, their practical application was limited due to particle growth during reduction of TiO_2 precursor. Especially in fuel cells, electrodes need large specific surface area, thus nanostructures are necessary.

We succeeded in the synthesis of nanostructured reduced titanium oxides via a low-temperature reduction approach, which enabled reduction of TiO_2 nanoparticles without particle growth. Through detailed electron microscope analyses (Fig. 1a), the reaction was found to proceed topotactically to form a corundum phase from rutile phase. Interestingly, the reduced phase thus obtained exhibited metallic conduction (Fig. 1b). Since the reduction method proceeds topotactically, rod-shaped nanostructured TiO_2 was also successfully converted into reduced one (Fig. 1c). Furthermore, the reduced TiO_x was proved to work as a corrosion-resistant electrode in acidic solution (Fig. 1d) up to 1.8 V *vs.* NHE. These results strongly indicate their application as electrode materials alternative to precious metals.

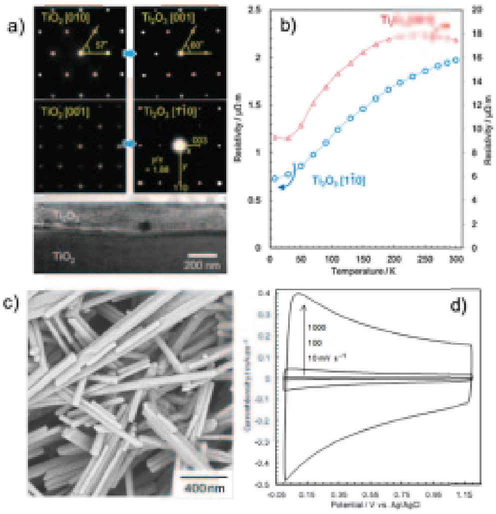

Fig. 1. (a) TEM images for revealing the topotactic reduction of TiO_2 to be Ti_2O_3. (b) Electron resistance characteristics showing (semi-)metallic behavior. (c) SEM images of reduced rod-shaped TiO_2. (d) Electrochemical response in acidic solution showing high chemical and electrochemical stability.

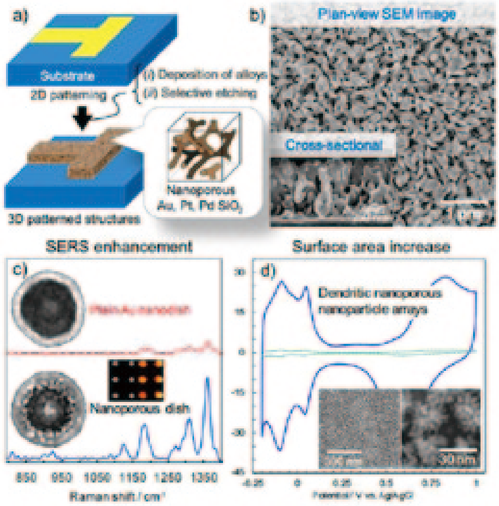

Fig. 2. (a) Schematic illustration of the method for arranging nanostructured materials at nano- or micrometer scale. (b) 3D grown nanoporous Au electrode. (c) Dish-shaped Au modified with manoporous Au. (d) Nanoporous Pt grains packed on Si substrate.

(2) Technology for arranging nanomaterials.[4-6]

Nanoporous materials are of great importance in a variety of applications such as heterogeneous catalysts because of their large specific surface area and tuneable porosity. We proposed an approach for rationally designing nanoporous materials on a substrate by lithography, alloy deposition and selective dissolution (Fig. 2a). The physical processes (*i.e.*, lithography and sputtering) were used to design shapes and arrangements of nanostructures, and the chemical dissolution process was used to form nanopores inside the nano-patterns. This approach enabled synthesis of a variety of nanoporous materials arranged on a substrate. (*i*) 3D-grown nanoporous Au layer (Fig. 2b) was deposited on microelectrode arrays. (*ii*) Dish-shaped Au nanostructures modified with nanoporous Au (Fig. 2c) was proved to improve SERS activity. (*iii*) Highly packed nanoporous Pt particles (Fig. 2d) effectively increased surface area of Pt electrode. (*iv*) Nanoporous SiO_2 disks seem to be useful for sensor applications.

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Theoretical Research on Electronic Properties of Nano-Carbon Systems and Atomically Thin Materials

MANA Independent Scientist Katsunori WAKABAYASHI

1. Outline of Research

Our research target is to theoretically reveal the peculiar electronic, magnetic, transport and optical properties in nanoscale materials and atomically thin films such as graphene, graphene nanoribbons, BC3 and MoS2 using theoretical and/or computation method. Their electronic properties show the strong thickness dependence, i.e. number of layers. For example, the electronic states of graphene are described by the massless Dirac Fermion in sharp contrast with the conventional two-dimensional electron gas on the semiconductor devices. However, multi-layer graphenes possess ordinal non-Dirac electronic properties.

In further, the miniaturization of the electronic devices composed of graphene or/and atomically thin films inevitably demands the clarification of nanoscale edge effects on the electronic structures, electronic transport and magnetic properties of those systems. We have already shown that the presence of edges in graphene has strong implications for the low-energy spectrum of the **π**-electrons. It was shown that ribbons with zigzag edges possess localized edge states with energies close to the Fermi level resulting in the spin polarization near the edge.

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 and atomically thin 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) Development of Analytic Method.[1-2]

The development of analytic method for massless Dirac Fermion systems is necessary not only for improvement of computational code but also for the intuitive understanding of quantum phenomena in the system. Recently we have succeeded to derive the full spectrum and corresponding wave function of graphene nanoribbons within the tight-binding model using wave-mechanics approach and transfer matrix approach. These analytical approaches revealed the scattering mechanism of pseudospins near the graphene edges. The states of pseudospins are conserved in the scattering process at the armchair edge, however the states of pseudospins are flipped in the scattering process at the zigzag edge. This striking difference in the scattering process of pseudospins at the graphene edges are decisive in the response of Raman spectroscopy and Berry's phase structures at the low-energy electronic properties of graphene near the edges.

(2) Electronic states of graphene corner edge and magic corner angle.[3-4]

The electronic states of graphene corner edge are of crucial issues from the experimental point of view, because the edge structures are relevant with the structural stability of the system. Recently we have studied the electronic states of semi-infinite graphene with a corner edge. The 60, 90, 120, and 150° corner edges are examined. We have numerically studied the local density of states (LDOS) on the basis of a nearest-neighbor tight-binding model using Haydock's recursion method. It was found that edge localized states appear along a zigzag edge of each corner edge structure except for the 120° case. This magic angle was analyzed within the framework of an effective mass equation.

(3) Hole doping effect on edge magnetic states.[5]

Graphene nanoribbons present an ideal platform for tweaking their unique electronic, magnetic and mechanical properties by various means for potential next-generation device applications. However, such tweaking requires knowledge of the electron-electron interactions that play a crucial role in these confined geometries. We have investigated the magnetic and conducting properties of zigzag edge graphene nanoribbons (ZGNRs) using the many-body configuration interaction (CI) method on the basis of the Hubbard Hamiltonian. For the half-filled case, the many-body ground state shows a ferromagnetic spin-spin correlation along the zigzag edge, which supports the picture obtained from one-electron theory. However, hole doping reduces the spin and charge excitation gap, making the ground state conducting and magnetic. We also provide a two-state model that explains the low-lying charge and spin excitation spectrum of ZGNRs. An experimental setup to confirm the hole-mediated conducting and magnetic states is discussed.

(4) Anomalous energy-gap behaviour of armchair BC_3 ribbons due to enhanced π-conjugation.[6]

The effect of edge passivation on armchair BC_3 ribbons is studied by first-principles calculations. The removal of passivating hydrogen from the edge boron atoms provides higher stability and makes the narrower ribbons metallic due to the enhanced π-conjugation along the edge. However, an increase in the ribbon width results in an unprecedented metal-to-semiconductor transition.

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Surfactant-Assisted Solution-Phase Synthesis of Nanoporous Metal Particles with Various Architectures

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.[1-6)]

Mesoporous metal particles have attracted much attention for years because of their beneficial uses as catalysts. The porous particles provide high surface area and a large number of edges and corners, which are important factors for catalytic applications. In spite of the recent advancements in synthesizing porous nanoparticles, complex and multistep procedures and/or high temperature and pressure conditions are required for the preparation of nanoporous metals.

Hence, we focused on designing a straightforward solution phase approach for the high yield synthesis of nanoporous particles with uniform size and morphology. All the nanoporous structures can be simply synthesized by purposefully changing the synthetic parameters including precursor composition (e.g. type and concentration of metal salts and surfactants, and pH) and synthetic conditions (e.g. synthetic temperature and ultrasonic irradiation). 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

Fig. 1 shows SEM and TEM images of the obtained hollow mesoporous Pt-Ru particles with a uniform particle size of around 160 nm, synthesized under typical synthetic conditions. From high-resolution SEM images, well-defined mesoporous architecture was observed over the entire area of the external surface. The average shell thickness was around 28 nm. The mesopores were spherical shapes and remarkably uniform in size (The average pore size was around 8-9 nm). The corresponding N_2 sorption result gave a high BET surface area of 41 $m^2 \cdot g^{-1}$. After addition of Ru to the precursor solution, the Ru content in the final product was increased up to 15 atomic%, as determined by inductively coupled plasma (ICP) analysis. As shown in Figure 1b, a bright center was surrounded by a dark peripheral area. Such a strong contrast clearly indicates the formation of a hollow interior structure. High resolution TEM images clearly showed the lattice fringes with a d spacing of 0.23 nm, corresponding to the (111) planes of a face center cubic (fcc) crystal structure. Selected-area electron diffraction (ED) patterns taken from one particle revealed the concentric rings attributed to (111), (200), (220) and (311) planes of a fcc crystal, indicating the polycrystalline nature. Line-scanning elemental mapping showed that both Pt and Ru were concentrated at the peripheral area according to the morphology of hollow particles. The uniform distribution of both elements throughout the hollow particle also confirmed the formation of a Pt-Ru alloy structure.

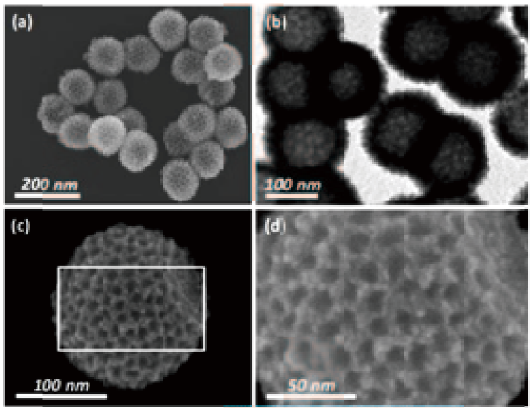

Fig. 1. (a, c, and d) SEM and (b) TEM images for hollow mesoporous Pt-Ru particles, named as mesoporous metallic cells, prepared under the typical conditions. (d) Enlarged image of the square area of (c).

As a preliminary demonstration of electrocatalytic activity of the prepared samples toward the methanol oxidation reaction (MOR), the electrocatalytic activity of several samples with different shell thicknesses was examined using a cyclic voltammetry method in 0.5 M H_2SO_4+0.5 M methanol electrolyte. For comparison, electrocatalytic activity of hollow mesoporous Pt particles (with 13 nm shell thickness) and commercial Pt black was measured as well. All the obtained currents were normalized with respect to the loaded amount of sample. Hollow mesoporous Pt-Ru particles with a thin shell (around 13 nm) showed the highest current density (384 $mA \cdot mg^{-1}$). This value was much higher than those of other samples, such as hollow mesoporous Pt (89 $mA \cdot mg^{-1}$), commercial Pt black (82 $mA \cdot mg^{-1}$), and commercial activated carbon with Pt nanoparticles (136 $mA \cdot mg^{-1}$), and also around twice higher than those of dendritic Pt-Ru spheres with almost the same Pt-Ru composition.

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Comprehensive Development of MSS-type Nanomechanical Sensors

MANA Independent Scientist Genki YOSHIKAWA

1. Outline of Research

The demands for new sensors are rapidly growing in various fields; medicine, security and environment. Nanomechanical sensors have potential to contribute to these global demands owing to their intrinsic versatility — detecting fundamental parameters, such as "volume" or "mass". Since all molecules have "volume" and "mass", nanomechanical transduction of them into detectable signals can realize label-free and real-time measurements of virtually any kind of target specimen. Based on the newly developed platform "Membrane-type Surface stress Sensor (MSS)," we are now trying to realize useful nanomechanical sensors which can fulfill the practical requirements, such as portability, low-cost, ease of use, in addition to the basic specifications, *e.g.,* high sensitivity.1)

2. Research Activities

(1) Second generation Membrane-type Surface stress Sensors (2G-MSS) with a 2D array.

Recently, we made comprehensive optimization of a piezoresistive cantilever sensor and developed a new platform; MSS with a high sensitivity comparable with that of optically read-out cantilever sensors.1) To demonstrate the capability of MSS for the multi-dimensional array, we fabricated the second generation MSS (2G-MSS) with a two dimensional array (Fig. 1. (a)).2) The implementation of various modifications in design and microfabrication led to further enhancement of sensitivity, reaching more than ~100 times higher sensitivity compared to that of the standard piezoresistive cantilever (Fig. 1. (b)).2)

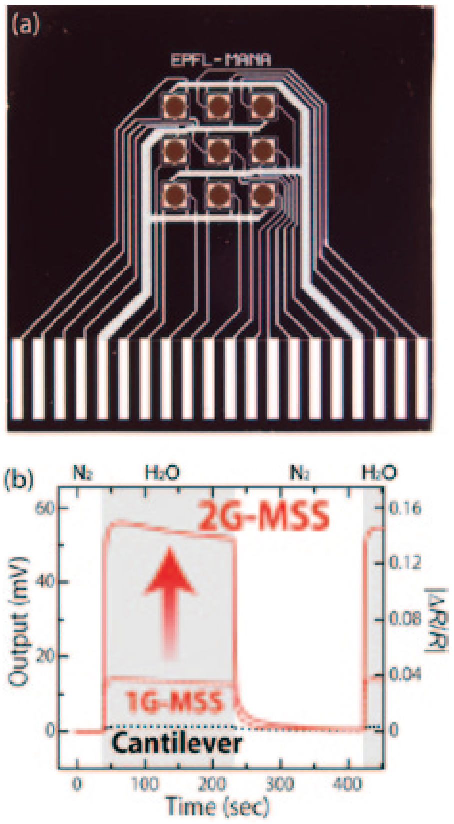

Fig. 1. (a) Photograph of the fabricated 2G-MSS chip with a 2D array. (b) Obtained output signals from the 2G-MSS chip (red solid line), 1G-MSS chip (red dashed line), and standard piezoresistive cantilever (black dotted line).

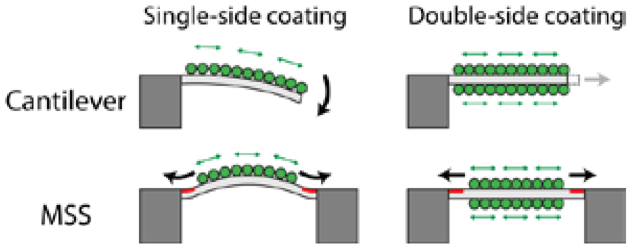

Fig. 2. Schematic side views of a cantilever and an MSS with single- and double-side-coatings, respectively.

(2) Double-side-coated MSS for One-chip-one-channel Setup.3)

For practical applications, one of the major issues of nanomechanical sensors is the difficulty in coating receptor layers on their surface to which target molecules adsorb or react. The MSS provides an effective solution to this coating issue by means of double-side-coating. While a cantilever-type sensor requires a single-side-coating to have measurable deflection, MSS has been found to yield reasonable signals even with double-side-coatings (Fig. 2), allowing almost any kind of coating technique including dip-coating methods. This feature of MSS was verified by both finite element analysis (FEA) and experiments. In addition, a simple hand-operated dip coating method was demonstrated as a proof-of-concept, achieving highly consistent coating layers without any complex instrumentation. As the double-side-coating is compatible with batch protocols, such as, dip coating, the double-side-coated MSS represents a new paradigm of "one-chip-one-channel (channels on a chip are all coated with the same receptor layers)" shifting from the conventional "one-chip-multiple-channel (channels on a chip are coated with different receptor layers)" paradigm.

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Fullerene-Based Nanomagnet

ICYS-MANA Researcher **Fatin HAJJAJ**

1. Outline of Research

Fullerene-based nanomaterials with a paramagnetic character are important motifs for the realization of molecular magnets, where emergent magnetic properties are realized by the collective spin states of the molecular components. Recently, paramagnetic endohedral metallofullerenes (EMFs) have attracted wide interest due to their potential applications in magnetic materials and quantum information processing. In this respect, a variety of spin-active EMF-based complexes have been developed by different approaches, where new magnetic properties are achieved by intramolecular spin coupling. In view of its elusive structure and alluring electron spin resonance (ESR) spectrum, spin-spin coupling interaction involving paramagnetic $Sc_3C_2@C_{80}$ is an attractive subject. Recent results showed that exohedral functionalization of $Sc_3C_2@C_{80}$ can effectively tune its paramagnetic properties. However, as the chemical modification alters the electronic and geometrical structure of pristine $Sc_3C_2@C_{80}$, other approaches become desirable. Herein we report the first spin-active supramolecular complex featuring pristine $Sc_3C_2@C_{80}$ as a molecular guest. Our research incentive on utilizing $Sc_3C_2@C_{80}$ stemmed from that fact that its paramagnetic character originates from a radical evenly localized on the endohedral Sc_3C_2 moiety. We envisioned that the paramagnetic properties of $Sc_3C_2@C_{80}$ can be altered by wrapping with paramagnetic *Cyclo*-$[P_{Cu}]_2$ (Fig. 1). *Cyclo*-$[P_{Cu}]_2$, designed for hosting $Sc_3C_2@C_{80}$, bears alkyl side chains with olefinic termini that can be transformed into its caged analogue *cage*-$[P_{Cu}]_2$ by intramolecular ring-closing olefin metathesis (Fig. 1). From our previous experiences on higher fullerenes and short-spaced cyclodimeric metalloporphyrin hosts, we assumed that only *cage*-$[P_{Cu}]_2$, after confining $Sc_3C_2@C_{80}$, would allow such a large fullerene to be located in its tetrapodal cavity without dissociation in the solid state.1) Of further interest, the resultant caged cluster, *cage*-$[P_{Cu}]_2 \supset Sc_3C_2@C_{80}$ (Fig. 1), displayed a spin coupling profile quite different from the ones observed for its molecular components.2)

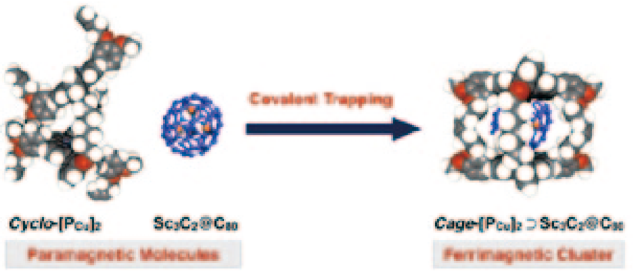

Fig. 1. Schematic illustration of the structures of Cu(II) porphyrin dimer (*cyclo*-$[P_{Cu}]_2$) and endohedral metallofullerene ($Sc_3C_2@C_{80}$) and their transformation into a ferrimagnetic complex.

2. Research Activities

The host framework was synthesized as a zinc porphyrin form by the fluoride-mediated coupling of the corresponding bromoalkylated zinc porphyrin with a zinc porphyrin bearing silylated phenol functionalities, and unambiguously characterized by MALDI-TOF mass spectrometry and ^1H NMR spectroscopy. Successive acid-triggered demetalation followed by copper metalation of porphyrin moieties afforded *cyclo*-$[P_{Cu}]_2$ almost quantitatively. Spectroscopic titration of *cyclo*-$[P_{Cu}]_2$ with $Sc_3C_2@C_{80}$ in toluene at 25 °C resulted in a red shift of the Soret absorption band of *cyclo*-$[P_{Cu}]_2$ from 418 to 424 nm with a decrease in intensity, characteristic of complexation with fullerene. Next, *cyclo*-$[P_{Cu}]_2 \supset Sc_3C_2@C_{80}$ was subjected to ring-closing olefin metathesis. MALDI-TOF mass spectrometry of the product (*cage*-$[P_{Cu}]_2 \supset Sc_3C_2@C_{80}$) showed only a single peak due to the host/guest complex. In sharp contrast, *cyclo*-$[P_{Cu}]_2 \supset Sc_3C_2@C_{80}$ in MALDI-TOF mass spectrometry underwent complete dissociation, affording the molecular ion peaks of *cyclo*-$[P_{Cu}]_2$ and $Sc_3C_2@C_{80}$. Hence, $Sc_3C_2@C_{80}$ is indeed trapped by *cage*-$[P_{Cu}]_2$ and not allowed to escape from its tetrapodal cage.

In order to investigate the possibility of spin-exchange coupling between the two copper atoms on *cage*-$[P_{Cu}]_2$ and the trapped $Sc_3C_2@C_{80}$, we conducted ESR spectral study on *cage*-$[P_{Cu}]_2 \supset Sc_3C_2@C_{80}$ and its molecular components as references in frozen solutions. A chlorobenzene solution of *cage*-$[P_{Cu}]_2$, frozen at −263 °C, displayed an ESR spectral feature analogous to that of a monomeric Cu(II) porphyrin species, indicating that the two copper-centered spins in *cage*-$[P_{Cu}]_2$ hardly interact magnetically with one another. Accordingly, the spin ground state of *cage*-$[P_{Cu}]_2$, as previously determined by electron spin transient nutation (ESTN) spectroscopy, is doublet.1) In sharp contrast, *cage*-$[P_{Cu}]_2 \supset Sc_3C_2@C_{80}$ displayed an ESR signal centred at 340 mT, whose position and pattern are essentially different from those of guest-free *cage*-$[P_{Cu}]_2$ and that of pristine $Sc_3C_2@C_{80}$. Such a drastic ESR spectral change of *cage*-$[P_{Cu}]_2$ after trapping $Sc_3C_2@C_{80}$ strongly suggests that the spins on *cage*-$[P_{Cu}]_2$ and $Sc_3C_2@C_{80}$ are coupled to form a new spin state. The ESTN spectral profile of *cage*-$[P_{Cu}]_2 \supset Sc_3C_2@C_{80}$ showed that its spin ground state is doublet. This means that the interaction between the host and guest components in *cage*-$[P_{Cu}]_2 \supset Sc_3C_2@C_{80}$ is ferrimagnetic. This is quite interesting, since the ferrimagnetic spin coupling is unprecedented for $Sc_3C_2@C_{80}$.2)

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Self-Assembled Monolayers Toward New Dynamic and Magnetoresistive RAM

ICYS-MANA Researcher Hicham HAMOUDI

1. Outline of Research

At the nanometer-dimension where the manipulation of electrons in the orbital levels is fundamental, the quantum physics is needed to control the nano-electronic features. The efficiency of the future quantum devices (QD) depends strongly on the homogeneous architecture of the nanocomposite. Systems based on the technology of self-assembled monolayers (SAMs) provide homogeneous materials, such as freestanding organic nanosheets or carbon nanomembranes (CNMs). Different theoretical studies show the significant role played by the class of molecular system consisting of organometallic half-metallic benzene-metal cluster sandwiched between carbon nanotube (CNT) or graphene contacts. The implementation of this type of architecture will open horizons for a class of polyvalent quantum materials for transport, storage, and computing. The objective of this research is to fabricate prototypes of molecular-based thin film for storing data, transporting and computing utilizing new hybrid materials based on molecules and ions metal interaction.

2. Research Activities

(1) Building block strategy.

The conjugate organic SAMs can provide all the ingredients to create new hybrid materials with novel functionalities out of the scope of traditional solid state devices, and this class of molecules contain very interesting electronic and magnetic properties, such as the existence of Giant magneto resistance (GMR) in phenyledithiolate molecules between nickel contacts[1] and electron transport by charge injections through different molecular orbital MOs.[2] The exchange protocols between dithiols-molecules such as BDMT and the metal ions make the implementation of the lateral and the vertical assembly codes possible. The sequential immersion of the substrate into the BDMT solution and M+ provide a multilayer SAMs as depicted in Fig. 1.

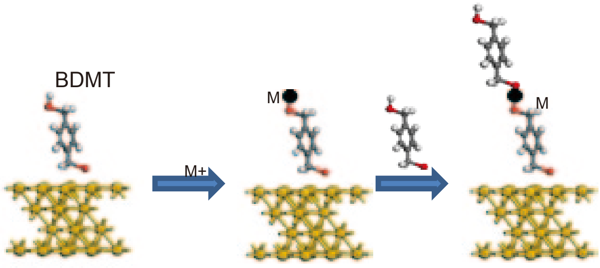

Fig. 1. BDMT-Ag-BDMT - Building block strategy.

(2) Freestanding Organometallic Nanosheets.

Using the bottom-up approach (see Fig. 1) I have built a new generation of materials considered as surfaces without bulk “freestanding organometallic nanosheets” with a nanometer thickness for the mono- and multi- layer sheets, and a lateral dimension in the millimeter range from cross-linked aromatic (BPD- M) self-assembled monolayer. After cross-linking of the (BPD-M) SAMs, the freestanding organometallic nanomembranes have been released by the dissolving of the underlying substrate or by scission of the anchor group-substrate bonds. Fig. 2 shows freestanding Carbon-metal nanosheets, which is one of the derivative products of the freestanding organometallic nanosheets.

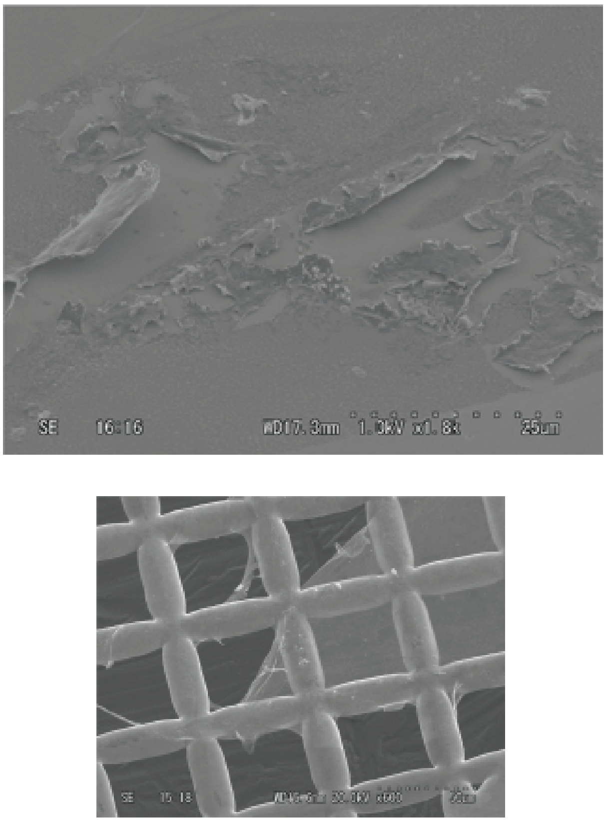

Fig. 2. (Top) BPD-Ni-BPD deposited on Si-SiO$_2$. (Bottom) BPD-Cu-BPD deposited on TEM grid.

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Nanostructured Coordination Polymers for Water Treatment and Biomedical Application

ICYS-MANA Researcher Ming HU

1. Outline of Research

Nowadays, environment problems and life science are attracting more and more attention among the world. Water treatment and drug delivery are two important topics which could be solved by materials scientists. Very interesting, both of the two different topics require materials with good adsorption capability, water stability and environmental friendly property. Therefore, it is of great interests to design materials to solve both of the problems. Crystalline coordination polymers (CCPs), as very famous microporous materials, show very high specific surface areas and large pore volumes which make them excellent candidates for water treatment and drug delivery.

Due to the obvious advantages, it is of fundamental and practical importance to fabricate CCPs with sophisticate structures for water treatment and drug delivery. The proposed work may result in materials with excellent properties in water treatment and drug delivery.

2. Research Activities

(1) *Syntheses of microporous metal-cyanide compounds nanocrystals.*

Kinetically-controlled synthesis was developed to fabricate microporous metal-cyanide compounds with well-defined morphologies. By using chelating agents, the kinetic of the crystallization process of microporous metal-cyanide compounds can be influenced significantly (Fig. 1).[1,2] Various kinds of nanostructures of microporous metal-cyanide compounds can be built via bottom-up process. Depending on the intrinsic crystal structure, the products were developed to nanocubes (when the crystal structures are cubic) or nanosheets (when the crystal structures are two-dimensional).

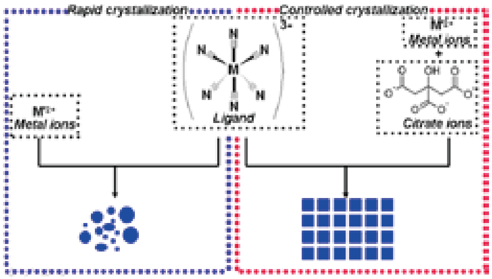

Fig. 1. Generation process of PB analogues.

(2) *Syntheses of microporous PBAs nanocrystals with heterogeneous nanostructures.*

We demonstrated an exquisite construction method to synthesize CPs with multiple hollow-based nanoarchitectures. Through step-by-step CP crystal growth and subsequent etching processes, various types of CPs with shell-in-shell, yolk-shell, and yolk-double-shell hollow structures can be synthesized for the first time (Fig. 2).[3] This type of nanoarchitecture is powerful for the exploration of alternative properties of CPs. The resultant hollow-based nanoarchitectures significantly alternated the gas sorption behavior and bring out interesting magnetic properties.

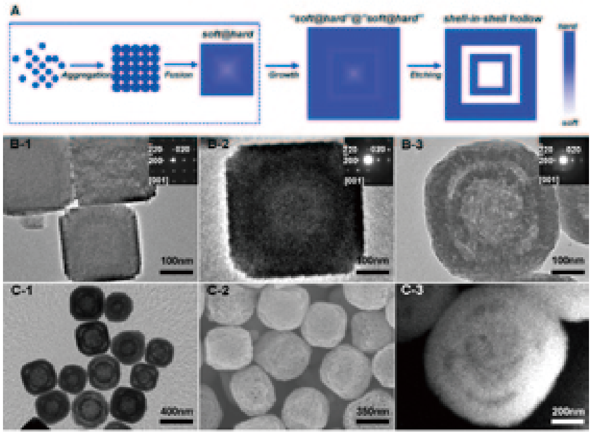

Fig. 2 (A) Schematic illustration for making shell-in-shell *FeFe* hollow particles. (B-1) TEM image of *FeFe* particles as the starting seeds. (B-2) TEM image of a 'soft@hard'@'soft@hard' *FeFe* particle grown on the seed. (B-3) TEM image of shell-in-shell hollow *FeFe* particle after chemical etching. (C-1) Low-magnified TEM image of shell-in-shell hollow *FeFe* particles after chemical etching. (C-2) SEM image of shell-in-shell hollow *FeFe* particles after chemical etching. (C-3) HAADF-STEM image of a shell-in-shell hollow *FeFe* particle.

(3) *Cs^+ removal of hollow MOF nanoparticles.*

We have investigated the Cs adsorption of hollow Prussian Blue analogue nanocrytals. We found that they can adsorb ten times more Cs^+ ions than commercial PB (Fig. 3).[4]

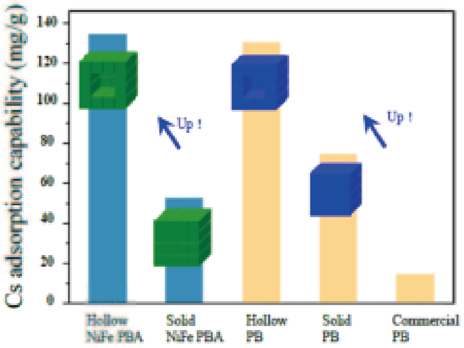

Fig. 3. Cs^+ adsorption capability of hollow MOF nanoparticle compared to solid and commercial ones.

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Supramolecular Nanomaterials with Switching, Sensing, and Dynamic Functions

ICYS-MANA Researcher Shinsuke ISHIHARA

1. Outline of Research

Materials emerge to demonstrate interesting functions when they are nano-structured, assembled, and organized. The purpose of my research is to design and synthesis of functional nanomaterials based on such 'supramolecular concept', which are available for energy, environmental, and nanotechnological applications. Typical examples are molecular switch,1) water sensor,2,3) clay-actuator,4) porous polymer,5) and exhaust catalyst.6) Details of some examples are shown blow.

2. Research Activities

(1) Molecular switch.1)

Porphyrin bearing 2,6-di-*tert*-butylphenol groups at 5 and 15 *meso*-positions demonstrate reversible photoredox interconversion between porphodimethene with drastic change of both molecular conformation and opto-electric property. The photoredox reaction proceeds only when both photoirradiation and chemical additives are applied, therefore, such character of AND-type logic gate gives rise to non-volatile and non-destructive readout memory (Fig. 1). The mechanism of photo-switching is proved to be photo-induced electron transfer by time-resolved laser photolysis and ESR measurements. Our results propose a simple and versatile strategy for producing photo-switchable macrocyclic compounds. Taking advantage of the ease self-assembling tendency for macrocyclic compound, we anticipate that our finding will lead to a new class advanced material suitable for bottom-up fabrication of molecular devices.

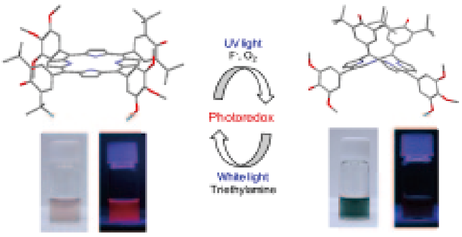

Fig.1. AND-type photo-switching of porphyrin derivative with drastic change of molecular conformation and opto-electric property.

(2) Water Sensor.2,3)

Quantitative analysis of contaminating H_2O in organic solvents is important in fundamental and industrial applications, especially in polar aprotic solvents which are used as solvents for water-flammable reagents. We found that oxoporphyrinogens (OxPs), a class of porphyrinoid, are available as colorimetric indicators for trace amounts of contaminating H_2O in tetrahydrofuran (THF) to a level of ~50 ppm by means of UV-Vis spectroscopy (Fig. 2). This makes a rapid and convenient method for analysing supposedly anhydrous THF prior to mixing with water-sensitive chemicals while, in turn, improving laboratory safety and reaction yields.

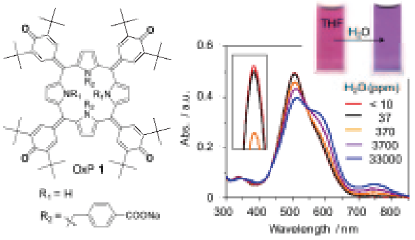

Fig.2. Colorimetric detection of trace water in THF using OxPs.

(3) Clay-actuator.4)

A particular type of LDH can homogeneously incorporate differently-sized alcohols at its interlayer space to form a self-assembled mono- or bi-layer (Fig.3). Unlike conventional ion-exchange-driven intercalation in clays, intercalated alcohol molecules are bound to the water contained in the LDH crystalline layers through weak hydrogen bonds permitting smooth molecular interdiffusion. This latter process ensures homogeneity of the self-assembly layer within LDH even if differently-sized alcohols are intercalated. Surprisingly, synchrotron-XRD proved that the interlayer distance of the LDH can be controlled with sub-Ångström precision by altering the mole ratio of the intercalated alcohols. Intercalated LDH not only provides a highly fluidic self-assembly layer for biomimetic applications, but also will contribute significantly to nanomanipulation of synthetic molecules or bio-macromolecules.

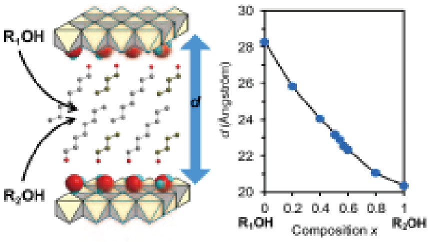

Fig. 3. Adjusting inter-layer space of LDH at sub-Ångström precision based on homogeneous intercalation of mixed alcohols.

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Atomic Field-Effect Transistor for Ultimate Electronics

ICYS-MANA Researcher Song-Lin LI

1. Outline of Research

With aggressive scaling down over four decades, the device miniaturization based on conventional planar lithography and processing has reached its physical limit in semiconductor industry. Currently, the over-shrunk gate length causes large stand-by current leakage and severe performance degradation in bulk silicon field-effect transistors (FETs). In the future, besides high-permittivity gate dielectrics and metal gate electrodes, the FETs also require ultrathin body (UTB), such as silicon-on-insulator channel or Fin-structure, in order to meet the stringent specifications of the International Technology Roadmap for Semiconductors. Although the advanced UTB structures can relieve the pressure of miniaturization for several years, the inevitable surface roughness between Si channel and SiO_2 dielectric, which causes unacceptable carrier scattering in few nanometer channels, remains unsolved. Hence, the two-dimensional semiconductors, such as MoS_2 monolayer, which combine both advantages of atomic thickness and flatness, represent an ultimate material for post-silicon microelectronics.

2. Research Activities

(1) Thickness Identification.

So far, there have been few rapid and nondestructive thickness characterization techniques for the inorganic atomic layers. A direct transfer of the well established schemes from graphene, such as optical contrast and Raman phonon position, to the inorganic atomic flakes seems not so successful.

We developed a unique and rapid thickness identification technique for atomic-scale layers on dielectric substrates based on interference Raman spectrum.[1] It is demonstrated that the Raman intensities for both the specimen and substrate layers can be quantified and well described in a common stacked experimental configuration. Unprecedentedly wide-range Raman data for atomic MoS_2 flakes (from 1 to ~120 layers) are collected to compare with theoretical models. We revealed that all intensity features can be accurately captured when including optical interference effect. Surprisingly, we found that even freely suspended chalcogenide few-layer flakes have a stronger Raman response than that from bulk phase. Importantly, despite the oscillating intensity of specimen spectrum versus thickness, the substrate weighted spectral intensity becomes monotonic. Combined with its sensitivity to specimen thickness, we suggest this new quantity can be used to rapidly determine the accurate thickness for atomic layers (Fig. 1a).

(2) Electronic Transport.

Based on the accurate information on sample layers, we performed combined experimental and theoretical studies, and employed the channel thickness as a unique clue to clarify the underlying scattering mechanisms in atomic FETs.

Due to the analogue "skin effect" of electrical carriers to the gating dielectric, theoretically, the Coulomb impurities at the lower surface (i.e., MoS_2/SiO_2 interface) dominate the scattering events for thick channels, while both the Coulomb impurities at both the upper (i.e., MoS_2/air interface) and lower surface are the leading scatters in ultrathin channels. Experimentally, the carrier mobility changes by one order of magnitude, increasing from ~10 to 200 cm^2/Vs in pristine SiO_2/MoS_2/air structures, as the MoS_2 channel increases from monolayer to bulk. A careful comparison between experiment and theoretical calculation indicates that the high-density (~10^{13} cm^{-2}) Coulomb impurities at the lower surface are the leading scatters in the atomic channels (Fig. 1b). Besides, the substitute of "dirty" SiO_2 with flat and dangling-bond free h-BN substrates can significantly reduce the Coulomb scattering and enhance the FET performance. The result highlights the critical role of substrate quality in electrical transport and provides direct guidance in performance improvement in atomic-scale FETs.

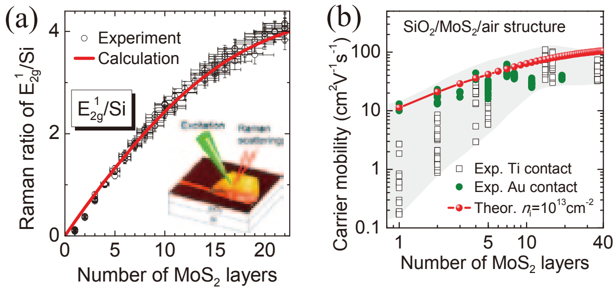

Fig.1. (a) Comparison between calculation and experiment for intensity ratio of the MoS_2 E_{2g}^1 (~ 383 cm^{-1}) Raman mode to that of the Si substrate (520 cm-1). This new quantity can be used as a unique criterion for counting the number of layers (NLs) for atomic sheets. The errors for the assgined NL values (by AFM) and intensity ratios are 10% and 5%, respectively. (b) Thickness-dependent carrier transport for the atomic MoS_2 layers, which is used to uncover the dominant carrier scattering mechanism. Both experimental and theoretical results are shown.

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High-Efficiency Photo-Electric Energy Conversion Devices Based on $In_xGa_{1-x}N$

ICYS-MANA Researcher Liwen SANG

1. Outline of Research

The direct-bandgap III-Nitride semiconductor family span the widest spectral range among all the semiconductors, ranging from the infrared (InN at 0.65 eV) through the visible and the ultra-violet (UV) (GaN at 3.42 eV) to the deep UV region (AlN at 6.2 eV). They also have the advantages of high drift velocity, high radiation resistance, large absorption coefficient, and high carrier mobility. These superior properties provide the promising applications in the high-efficiency photo·electricity energy conversion devices, such as solid-state lighting, high-performance photodiodes and ultra-high efficiency (~50%) solar cells.

Compared to the short-wavelength devices using GaN, AlN, and low-In $In_xGa_{1-x}N$, long-wavelength devices using In-rich $In_xGa_{1-x}N$ (x>40%) are less reported, which hinders the development of ultra-high efficiency solar cells and high-brightness light emitting diodes. This is because of the poor quality of In-rich $In_xGa_{1-x}N$ thick film and *p*-type doping. We aim to fabricate InGaN-based devices with a high In composition and achieve the high-efficiency photo·electricity conversion by using novel concepts from materials and devices.[1-3]

2. Research Activities

(1) World-record InGaN-based visible-blind photodiodes.

Ultraviolet (UV) sensors working in the visible-blind UV-A region (320-400 nm) have several applications, including flame detection, radiation analysis, biomedicine and environment monitoring, etc. In some cases such as the flame detection, thermally stable detectors with high performance are required. Currently, Si-based photodiodes are widely used to detect optical energy in the UV-A to visible region, while the performance of these devices is inadequate due to their narrow bandgaps. InGaN-based photodiodes offer an alternative and potentially better approach for detecting UV-A light due to their superior characteristics. A high-performance photodetectors fabricated on high-quality InGaN film by introducing a superwide bandgap calcium fluoride (CaF_2) insulation layer is reported, as shown in Fig. 1. The dark current is drastically reduced by six orders of magnitude with the introduction of this novel insulator, resulting in an extremely high discrimination ratio larger than 10^6 between UV and visible light. The photodetector is demonstrated to work at high temperatures up to 523 K. Both the electrical and optical properties are maintained at high temperatures. The responsivity is improved to be as high as 5.6 A/W at -3 V under 523 K, which is very desirable for high-temperature application.

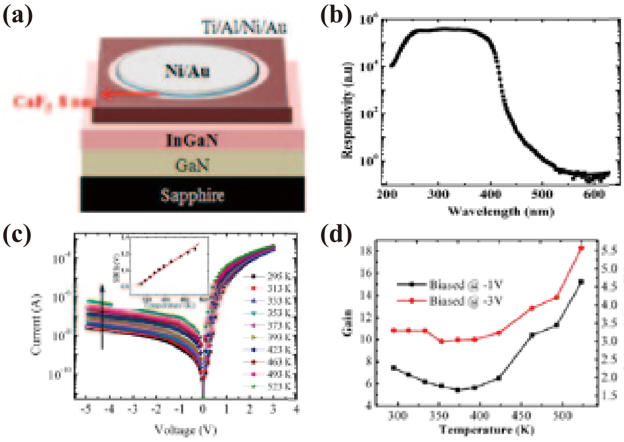

Fig. 1. Optical and electrical properties of InGaN photodiodes up to 523 K.

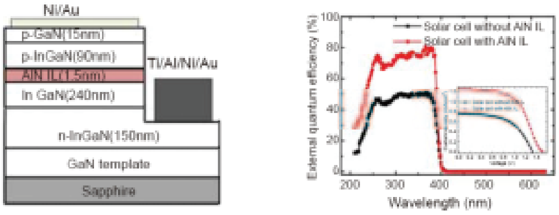

Fig. 2. Novel structure and photovoltaic property of InGaN solar cell.

(2) High quantum efficiency InGaN-based solar cells.

The power conversion efficiency of a multi-junction solar cell based on InGaN was expected to be approaching 62% according to the balance modeling estimation. Up to now, most of the reported InGaN solar cell utilized *p*-GaN rather than *p*-InGaN in the *p-n* junction structure with a low-In content active region (around 10%) due to the difficulty in the achievement of high-quality *p*-InGaN with a high In content. However, *p*-GaN exhibits a lower hole concentration, inefficient optical absorption, and opposite piezoelectric polarization in the *p-n* junctions. To improve the conversion efficiency, all InGaN-based solar cell is proposed. By using a strain-modulated two layer structure, the hole concentration of *p*-InGaN was improved to be more than $10^{18}/cm^3$, which is much higher than that of *p*-GaN. A super-thin AlN layer is inserted between the active region and *p*-type region to improve the photovoltaic property (Fig. 2). The dark current is markedly decreased by more than two orders of magnitude and the short-circuit current density is increased, leading to a doubled conversion efficiency compared to the conventional structure. The external quantum efficiency is improved to be close to 80%, which is the highest ever reported for InGaN-based solar cell (Fig. 2).

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Distinct Mechanical Behaviors of Si NWs Under Tension and Bending Revealed by In Situ TEM

ICYS-MANA Researcher Dai-Ming TANG

1. Outline of Research

Si NWs have attracted wide-spread research interest because of their unique properties and broad applications. A clear understanding on the mechanical properties and behaviors is vitally important for their reliable design and fabrications. Therefore, many studies have been conducted to elucidate the deformation and fracture mechanisms of Si NWs. However, controversial results have been reported with respect to the basic question: Are Si NWs brittle or ductile at room temperature?

In our study, we adopted an in situ TEM technique to investigate the mechanical properties and behaviors of Si NWs under both uniaxial tension and bending loading conditions. Compared with other techniques, in situ TEM enables direct and real-time observation of structural alternations under measurements with atomic resolution. We found that the mechanical behaviors are strongly dependent on the loading conditions and corresponding stress states.[1)]

2. Research Activities

(1) Brittle mechanical behaviors under tension.

Direct tensile tests on the Si NWs were conducted by using a TEM-AFM platform (Nanofactory, Fig. 1a). A typical strain-stress curve is shown in Fig. 1b, presenting a linear elastic deformation before an abrupt drop of the stress caused by the nanowire failure at about 4.6%. The measured Young's modulus was ~201 GPa which is close to that of a bulk Si in the [111] direction (187 GPa). The ultimate tensile strength was calculated to be ~8.7 GPa. A HRTEM image of a fracture surface is demonstrated in Fig. 1c, it is atomically flat and perpendicular to the axial direction. Although atomic steps could be seen occasionally, no necking or sliding was observed. Therefore, the Si nanowires are brittle under tension.

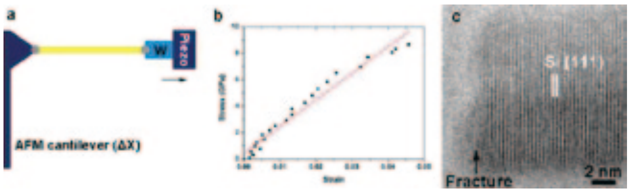

Fig. 1. (a) Schematic illustration of the tensile experimental configuration. (b) A typical strain-stress curve illustrating a linear elastic deformation until abrupt failure. (c) A HRTEM image of the Si NW fracture surface.

(2) Ductile behaviors under bending.

Bending tests were carried out to get a comprehensive assessment of the mechanical behaviors of Si NWs (Fig. 2). A crack was found at the tensed side when the bending strain reached about 20%. Under further bending, the crack became wider, however, even at the bending strain of 38.7%, the nanowire did not fail completely. The crack did not propagate through the whole nanowire, but became blunt at about the middle of the cross-section. In contrast to the crack on the tensed side, the structure on the compressed side became amorphous. In addition, dislocations were found around the severe deformation area along with the atomic steps on the surface, indicating the nucleation and movements of dislocations.

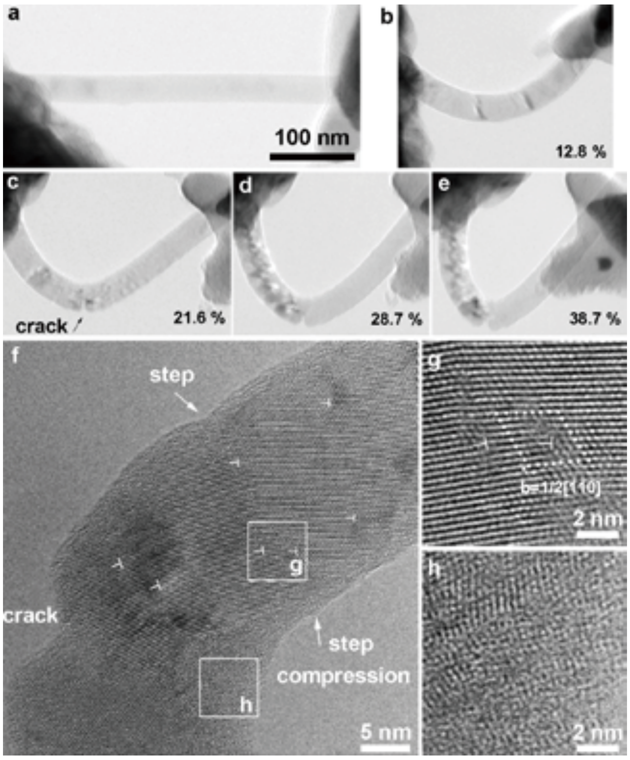

Fig. 2. In situ TEM bending test on a single Si NW with a diameter of 25.3 nm. (a-e) TEM images of the bending process. (f) A HRTEM image of the Si NW in (d). (g-h) HRTEM images of dislocations and the amorphized area.

The distinct mechanical behaviors under tension and compression could be understood by introducing the stress state parameter ($\alpha = \frac{\tau_{max}}{S_{max}} = \frac{\sigma_1 - \sigma_3}{2[\sigma_1 - \nu(\sigma_2 + \sigma_3)]}$), which is the ratio of maximum shear stress and maximum normal stress of a stress state. The parameter is calculated to be 0.5 and ~2 under uniaxial tension and compression states, respectively. Our finding of stress state dependent mechanical properties helps understanding the puzzling controversy over the mechanical behaviors of Si NWs.

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Oxygen Diffusivity in Ba-Fe-Based Perovskite

ICYS-MANA Researcher **Ken WATANABE**

1. Outline of Research

Mixed ionic and electronic conductors (MIECs) are the materials which exhibit both ion and electron (hole) conduction. For instance, when oxygen pressure differences are applied to the mixed oxide-ionic and electronic conductor, we can separate only oxygen from mixed gas without energy (Fig. 1). Due to its property, mixed oxide-ionic and electronic conductors are widely used as the electrode materials of solid oxide fuel cell (SOFC) and solid oxide electrolysis cell (SOEC), oxygen permeable membrane, membrane reactor for hydrogen production, gas sensor and so on. These applications are expected as cleaner, sustainable sources of energy and energy-saving process. These developments are one of the world wide challenges to overcome the environmental concern of global warming and the finite nature of fossil fuel reserves.

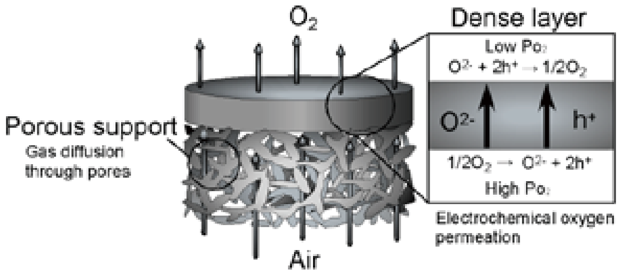

Fig. 1. Schematic drawing of the oxygen separation using the mixed conductor.

Recently, we found that $Ba_{0.95}La_{0.05}FeO_{3-\delta}$, (denoted by BLF) shows the high oxygen permeability under the oxygen partial pressure difference. However, there are some problems to overcome for its practical, such as high efficiency, long term stability, operating temperature and so on. To improve on the performance of mixed conductors, it is very important to control both oxygen diffusivity and electric conductivity.

It is well known that tracer diffusion is the effective method to evaluate the diffusivity of cation or anion in solid. In fact, we have already reported the oxygen and cation diffusion in metal oxide, by using the tracer diffusion and secondary ion mass spectrometry (SIMS).[1, 2] Here, in this research, we tried to evaluate the oxygen diffusivity in BLF, to design the high-efficiency mixed conductor. The tracer oxygen (^{18}O) was introduced into BLF by $^{18}O_2$/solid exchange reaction.

2. Research Activities

The oxygen vacancy diffusion coefficients calculated from tracer diffusion data are summarized in Fig. 2 as a function of the reciprocal temperature. The oxygen vacancy diffusion coefficients for 500, 600, and 700°C were estimated to be 3.1×10^{-6}, 6.2×10^{-6}, and 1.7×10^{-5} cm^2 s^{-1}, respectively. Note that diffusivity of BLF is one or two orders of magnitude higher than that of other reported Fe-based perovskite oxides. Moreover, those are higher than that of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$, which is the most promising candidate. In addition, the activation energy of oxygen vacancy diffusion was estimated to be about 0.53 eV. The activation energy of oxygen vacancy diffusion for BLF shows a good agreement with theoretical calculation for perovskite series (0.4-0.8 eV). This indicates that oxygen transport mechanism in BLF is explained well by the oxygen vacancy migration model. Thus, it was found that the diffusivity of BLF must be improved by the increasing of oxygen vacancy.

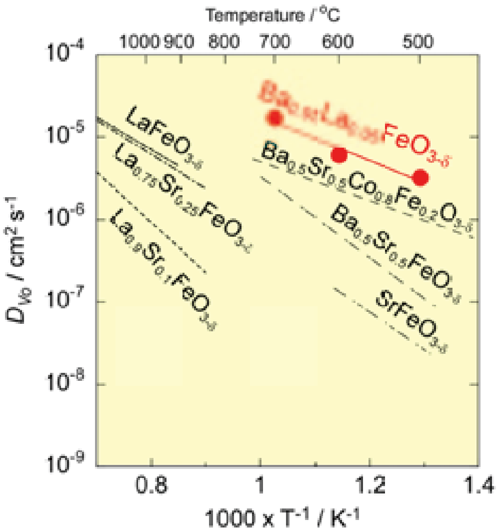

Fig. 2. Arrhenius plots of oxygen vacancy diffusion coefficients for BLF. For comparison, oxygen tracer diffusion coefficients for $La_{1-x}Sr_xFeO_{3-\delta}$, $Ba_{1-x}Sr_xFeO_{3-\delta}$, and $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.3}O_{3-\delta}$ are also shown.

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High-Performance Solar-Blind Photodetectors

ICYS-MANA Researcher **Tianyou ZHAI**

1. Outline of Research

One-dimensional (1D) inorganic nanostructures such as nanowires (NWs), nanobelts (NBs), and nanotubes (NTs) have stimulated numerous studies due to their importance in basic scientific research and potential technological applications. It is generally accepted that 1D inorganic nanostructures are ideal systems for exploring a large number of novel phenomena at the nanoscale and investigating the size and dimensionality dependence of functional properties. They are also expected to play important roles as both interconnects and key units in nanoscale electronic, optoelectronic, electrochemical, and electromechanical devices. Among many available nanoscale devices, the photodetectors are critical for applications as binary switches in imaging techniques and light-wave communications, as well as in future memory storage and optoelectronic circuits. In view of their high surface-to-volume ratios and Debye length comparable to their small size, 1D inorganic nanostructures have already displayed superior sensitivity to light in diverse experiments. We are aim to develop an effective approach to construct high-performance solar-blind photodetectors based on 1D ZnS, $In_2Ge_2O_7$, and Ga_2O_3 nanostructures.[1-6)]

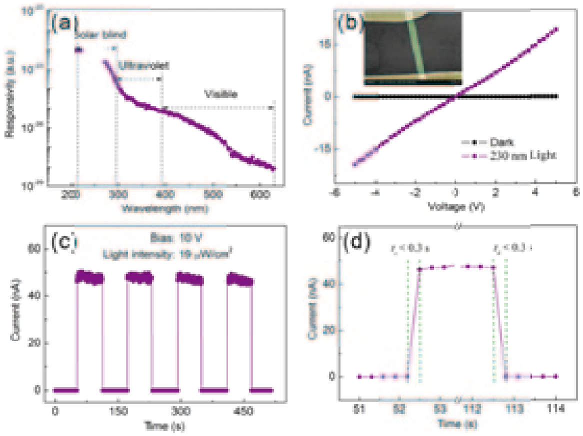

Fig. 1. Photoconductivity of $In_2Ge_2Ge_7$-nanobelt-device.

2. Research Activities

(1) $In_2Ge_2O_7$ nanobelt-based photodetector.

High-quality single crystalline $In_2Ge_2O_7$ nanobelts were synthesized by vapor transport process. Individual $In_2Ge_2O_7$ nanobelts were designed for solar-blind DUV photodetectors (Fig. 1). The detectors showed the ultrahigh photoconductive performance: 1) High sensitivity and selectivity towards the solar-blind spectrum. 2) Excellent stability and reproducibility. 3) Fast response and decay time (~ 2 ms). 4) Ultrahigh responsivity (3.9×10^5 A W^{-1}) and quantum efficiency (2.0×10^8 %). Up to now, these values are the best working parameters of solar-blind photodetectors. A power-law dependence of the photocurrent of $In_2Ge_2O_7$ nanobelts on light intensity was determined. Based on the dependence of photocurrent on environment and quantum efficiency on light intensity, ultrahigh performance of $In_2Ge_2O_7$ nanobelts was ascribed mainly to surface traps, 1D dimensionality, and high-quality single crystals. Present $In_2Ge_2O_7$ nanobelt photodetectors may find wide optoelectronic applications in optical sensing, switches, and communications.

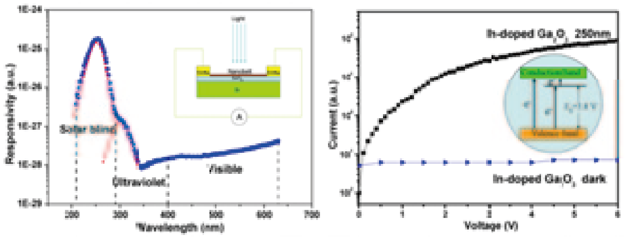

Fig. 2. Photoconductivity of In-doped Ga_2O_3 nanobelt device: (a) Spectral response; (b) I-V curve of the device under 250 nm illumination and in dark.

(2) In-doped Ga_2O_3 nanobelt-based photodetector.

We fabricated high-quality In-doped Ga_2O_3 nanobelts through a facile and effective thermal evaporation process. The detailed photoelectrical and electrical characteristics of individual In-doped Ga_2O_3 nanobelts have been investigated using a photodetector design and a field-effect transistor (FET) setup (Fig. 2). The In-doped Ga_2O_3 nanobelt-based devices have shown a higher photo-dark current ratio ($\approx 10^3$), responsivity (5.47×10^2 AW^{-1}), quantum efficiency (2.72×10^5 %) and conductivity (5.1×10^{-5} Scm^{-1}), i.e. much better figures compared with the undoped Ga_2O_3 nanobelt devices. In doping has led to significant improvements in the carrier transport and photoelectronic properties of Ga_2O_3 nanostructures, beneficial for the fabrication of high-performance future Ga_2O_3-based nanodevices.

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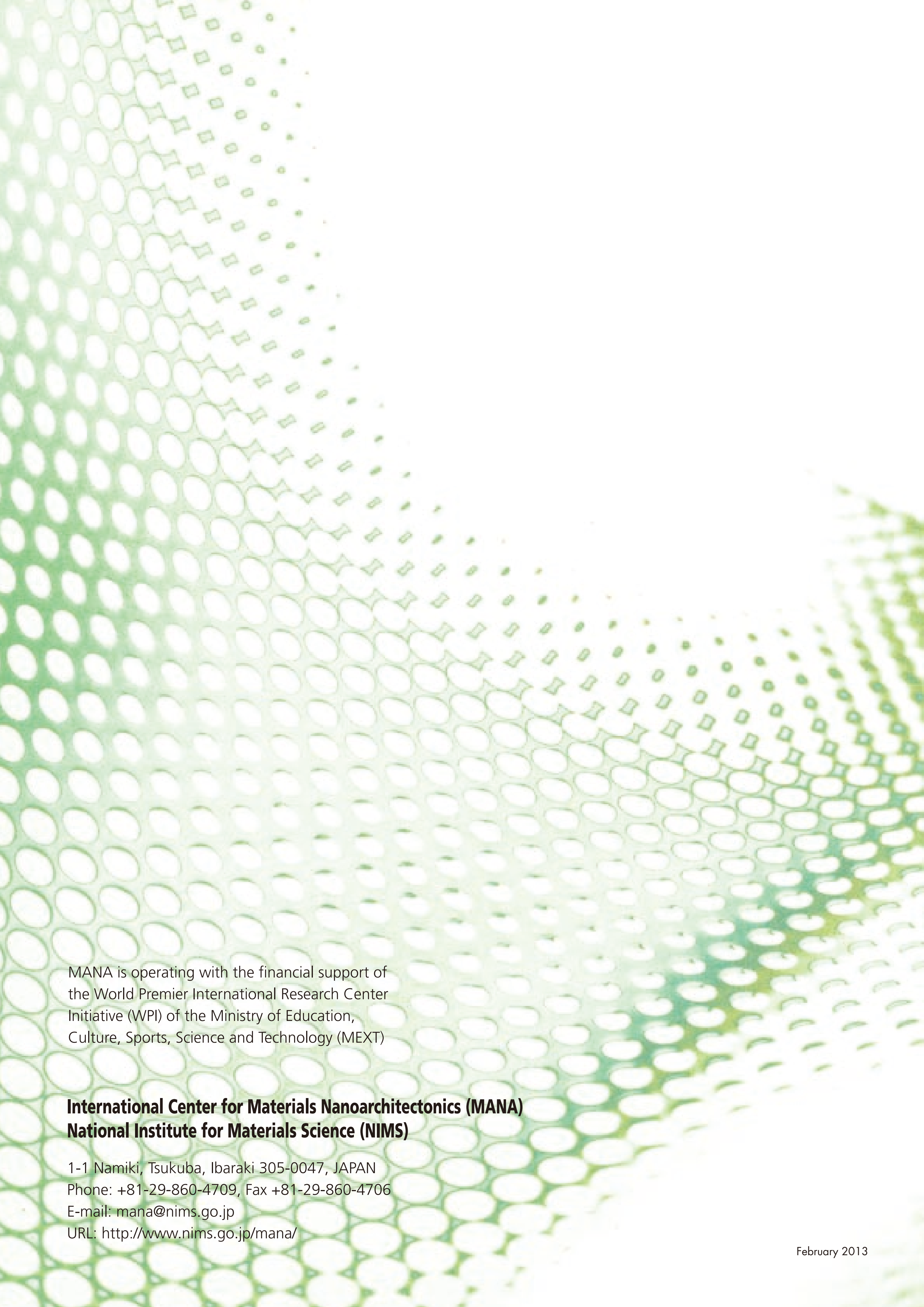

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