# MANA Progress Report Research Digest 2016



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

National Institute for Materials Science (NIMS)

# Preface

Masakazu Aono MANA Director-General NIMS

The International Center for Materials Nanoarchitectonics (MANA) was established in October 2007 as one of the initial five research centers in the framework of the World Premier International Research Center Initiative (WPI Program), which is sponsored by Japan's Ministry of Education, Culture, Sports, Science and Technology (MEXT). This year marks the tenth anniversary of the start of MANA. We are happy to see that MANA has grown to become one of the world's top research centers in materials science and technology and produced remarkable results in fields ranging from fundamental research to practical applications.

MANA is conducting research on the basis of the new concept "Nanoarchitectonics." This concept has been refined continuously by MANA's researchers and is now accepted around the world. As we follow this concept, MANA strives to extract the maximum value from nanotechnology for the development of appropriate materials for new innovative technologies. I humbly request your warm support as we continue our earnest efforts.

The MANA Progress Report consists of two booklets named "Research Digest 2016" and "Facts and Achievements 2016". This booklet "Research Digest 2016" presents MANA research activities and the other booklet "Facts and Achievements 2016" serves as a summary to highlight the progress of the MANA project.



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### Inorganic Nanosheets

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#### 1. Outline of Research

We aim at producing two-dimensional (2D) inorganic nanosheets as a unique class of nanoscale materials by delaminating various layered compounds through softchemical 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 colloidal nanosheets into multilayer or superlattice assemblies through solution-based processes (Fig. 1). Based on this novel approach with the nanosheets (soft-chemical 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...). In particular, 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) Modulation of photochemical activity of titania nanosheets via heteroassembly.<sup>1)</sup>

Films of titania nanosheets show photoinduced superhydrophilicity upon exposure to UV light, which is induced by photogenerated holes via the bandgap excitation. We found that the activity can be enhanced by combining reduced graphene oxide (rGO) as an electron transfer mediator. Titania nanosheets and GO were alternately assembled via sequential adsorption with polycation. The obtained films were exposed to UV light to reduce GO into rGO and to decompose polycation via photocatalytic action. The resulting system showed the higher wettability conversion activity by ~3 times (Fig. 2), which can be understood in terms of the transfer of photoexcited electrons to rGO to stabilize the charge separation.



Fig. 2. Efficient utilization of photogenerated carriers of titania nanosheets by designing the heterostructure.

# (2) Electrocatalysts of alternately stacked hydroxide nanosheets and graphene.<sup>2)</sup>

Superlattice composites, obtained through flocculation of Ni-Mn layered double hydroxide (LDH) nanosheets with GO/rGO, were tested as electrocatalysts for oxygen evolution reaction (OER). The intimate molecular-level heteroassembly of Ni-Mn LDH nanosheets with conductive rGO at an alternating sequence resulted in a small overpotential of 0.26 V and a Tafel slope of 46 mV per decade, which is much superior to as-exfoliated nanosheets (Fig. 3). The analyses of electrochemical activity surface area (ECSA) and impedance spectra clearly indicated that the superlattice structure was ideal in facilitating the migration/transfer of the charge and reactants, revealing the electrochemical energetics and mechanism behind the synergistic effect arising from molecular hybridization.



Fig. 3. OER catalytic activities of (r)GO/LDH nanocomposites in comparison with as-exfoliated GO and LDH nanosheets (NS).

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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. We are working in exploratory research for innovative materials and sensing systems based on supramolecular concept.<sup>1-9)</sup>

#### 2. Research Activities

(1) Hierarchically-Structured Fullerene C70 Cube for Sensing Volatile Aromatic Solvent Vapors (Fig. 1).<sup>7</sup>

We report the preparation of hierarchically-structured fullerene C70 cubes (HFC) composed of mesoporous C70 nanorods with crystalline pore walls. Highly crystalline cubic shape  $C_{70}$  crystals (FC) were grown at a liquid-liquid interface formed between tert-butyl alcohol (TBA) and C<sub>70</sub> solution in mesitylene. HFCs were then prepared by washing with isopropanol (IPA) of the FC at 25 °C. The growth directions and diameters of C70 nanorods could be controlled by varying washing conditions. HFCs perform as an excellent sensing system for vapor phase aromatic solvents due to their easy diffusion through the mesoporous architecture and strong  $\pi$ - $\pi$  interactions with the sp<sup>2</sup>-carbonrich pore walls. Moreover, HFCs offer an enhanced electrochemically active surface area resulting in an energy storage capacity one order of magnitude greater than pristine C70 and fullerene C70 cubes not containing mesoporous nanorods.



Fig. 1. Assembly of fullerene C70 into cube shaped crystals and its structural rearrangement into hierarchically-structured fullerene C70 cubes (HFC) with mesoporous nanorods.

(2) Supramolecular Differentiation for Construction of Anisotropic Fullerene Nanostructures by Time-Programmed Control of Interfacial Growth (Fig. 2).<sup>®</sup>

Supramolecular assembly can be used to construct a wide variety of ordered structures by exploiting the cumulative effects of multiple non-covalent interactions. However, the construction of anisotropic nanostructures remains subject to some limitations. Here we demonstrate the preparation of anisotropic fullerene-based nanostructures by supramolecular differentiation, which is the programmed control of multiple assembly strategies. We have carefully combined interfacial assembly and local phase separation phenomena using a combination of liquid-liquid interfacial assembly and homogeneous growth. Two fullerene derivatives, PhH and C12H, were together formed into selfassembled anisotropic nanostructures by using this approach. This technique is applicable for the construction of anisotropic nanostructures without the requirement of a complex molecular design, or complicated methodology.



Fig. 2. Supramolecular Differentiation for preparation of selfassembled anisotropic fullerene-based nanostructures.

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# **Inorganic Nanostructured Materials**

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#### 1. Outline of Research

Functionalization is an important way to breed new properties and applications for a material. Many methods have been developed for the functionalization of materials, including structural modulations (form low-dimensional, nanostructured, porous structures, etc.), hybridization with other components, chemical modifications, etc. We have developed a variety of functionalized BN materials, including BN porous monoliths, effective photocatalyst based on BN/Au/TiO<sub>2</sub> composite, etc. The detailed progress in this field was also comprehensively introduced and summarized in our recent review paper.

#### 2. Research Activities

(1) Template-free synthesis of boron nitride foam-like porous monoliths and their high-end applications in water purification.<sup>1)</sup>

We prepared BN-based porous monoliths (BNPMs) *via* a facile two-step template-free reaction. The resulting BNPMs exhibit a high specific surface area up to 1406 m<sup>2</sup> g<sup>-1</sup>. The material was applied for the highly efficient separation–adsorption purification of an oil/water system, demonstrating an excellent adsorption capacity of up to 71–98 vol %. Besides, they could remove rhodamine B (RB) and Cd (II) pollutants from an aqueous solution under a forced filtration–adsorption process, and thus are envisaged to be a fairly promising adsorbent for water cleaning (Fig. 1).



Fig. 1. (a, b) Photos of the adsorption process of a salad oil by using BNPM-1100 within 5 s. (c) After the adsorption was complete, the bulk BNPM-1100 could be conveniently clipped out from water.

(2) h-BN nanosheets as simple and effective additives to largely enhance the activity of Au/TiO<sub>2</sub> plasmonic photocatalysts.<sup>2)</sup>

We found the activity of Au nanoparticle-loaded P25

TiO<sub>2</sub> (Au/P25) plasmonic photocatalysts was enhanced up to 3 times by simply mixing Au/P25 with photocatalytically inactive h-BN nanosheets. We evaluated their catalytic performances by the oxidative decomposition of formic acid in water under visible light irradiation. Electron transfer from photoexcited Au/TiO<sub>2</sub> to the h-BN nanosheets and retardation of the charge recombination were considered as the main reasons for the enhanced photocatalytic activity of the composite (Fig. 2).



Fig. 2. (a) UV/Vis spectra of P25, Au/P25, BN, microporous titanate nanofiber (MPTNF) and titanosilicate zeolite (TS-1). (b) Photocatalytic activities for the oxidation of formic acid in water to  $CO_2$  over different samples under visible light irradiation ( $\lambda > 420$  nm).

#### (3) Functionalized hexagonal boron nitride nanomaterials: emerging properties and applications.<sup>3)</sup>

Our review presents an overview of the progresses in functionalized hexagonal boron nitride (h-BN)nanomaterials. We introduce h-BN structural features, physical and chemical properties, and emphasize on the developments of BN functionalization strategies and its emerging properties/applications. Different functionalization methods, including physical and chemical routes, are comprehensively described toward fabrication of various BN derivatives, hetero- and porous structures, etc. Novel properties of functionalized BN materials, such as high water solubility, excellent biocompatibility, tunable surface affinities, good processibility, adjustable band gaps, etc., have guaranteed wide applications in biomedical, electronic, composite, environmental and "green" energy-related fields.

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### Nano Electrics and Related Materials

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#### 1. Outline of Research

Ferroelectric materials exhibit spontaneous polarization (Ps) without the application of an electric field due to a lack of inversion symmetry and ionic bonds. To keep the charge neutrality level, there are abrupt changes at the polar surface, although the Ps is homogeneous and stable in bulk ferroelectrics.<sup>1)</sup> Guro et al. explained it in terms of screening charges compensation.<sup>2,3)</sup> The positive and the negative polar surfaces were compensated by electrons and holes, respectively. At the surface, the screening charges are generated both in and on the materials. Internal screening charges are mainly attributed to defects in the ferroelectric materials. The LiNbO<sub>3</sub>(LN), however, generates a greater external screening charge attributed to lower defect density. Also LN is a ferroelectrics material and has a large pyroelectric property (Ps), which is one of the unique properties of this material. Ps can be controlled by controlling the temperature, and can generate a huge number of electrons at the surface. These characters of LN suggest that the screening charge and pyroelectricity can be used for electron and voltage sources. This means that the LN surface can work as the energy harvesting electric energy. Especially if these charges are stored in a small area, LN will work as a small battery. In this report, we proposed that the Schottky barrier can work to store the surface charge. For this purpose, a Al/SiO<sub>2</sub>/LiNbO<sub>3</sub> structure is proposed and surface charge storage was demonstrated.

#### 2. Research Activities

A 0.5 mm thick Z-cut LN single crystal, whose polarization was inverted with a conventional electric poling technique, was used as a substrate. Subsequently 200 nm Al was deposited by e-beam method. At last, the lift-off process with e-beam lithography was employed to fabricate a regular hole array with a diameter of 2  $\mu$ m on the LN surface. To obtain a more stable charge accumulation some samples have a SiO<sub>2</sub> layer depositioned by chemical vapor deposition between Al and LN.

The surface structure and potential were investigated by atomic force microscopy which has Kelvin probe force microscopy (KFM) function. KFM was employed to evaluate the relative energy potential difference between the probe chip and a sample surface. A negative surface charge indicates a positive potential increase. The metal layer was grounded to the earth. The KFM measurements were performed in an Ar atmosphere to avoid surface contamination and additional charge.

The hole in the Al/LN structure showed a relatively negative potential regarding the Al layer. Al/LN should form a Schottky contact with LN. However, Al was strongly oxidized at the interface to form Al/Al<sub>2</sub>O<sub>3</sub>/LN and effective

charge storage was not performed. Therefore to enhance the charge stage effect, we require an insulator that has a wide band gap, a large band offset with a metal, and that acts as capacitor. Furthermore, the institution layer should have few defects to retain the screening charge effect. For this purpose,  $SiO_2$  was inserted between Al and LN.



Fig. 1. Sample surface image by AFM (a) and surface potential image by KFM (b).

Fig. 1(a) and Fig.1(b) show AFM and KFM images of Al/SiO<sub>2</sub>/LN structures, respectively.<sup>4)</sup> The electron affinity of SiO<sub>2</sub> is 0.6–0.8 eV, meaning that the potential of the metal layer should be larger than that of the LN layer. However, the potential in the hole area clearly increases, indicating that the insertion of a SiO<sub>2</sub> layer, which is a wide band gap dielectric layer of 9.0 eV, enhances the charge storage ability at the metal/LN interface. The relative potential between charge storage region and SiO<sub>2</sub> surface was approximately  $118\pm10$  meV. The electron density of the LN surface is estimated to be  $6\times10^7$  C/cm<sup>2</sup> based on the conversion from electron volt to electrical charge in coulombs, which is consistent with the reported surface charge of ferroelectrics generated by an intrinsic polarization effect and the screening charge of ferroelectrics.

In conclusion, we demonstrated surface charge localization generated by an intrinsic polarization effect and the screening charge of ferroelectrics. A Schottky formation acts as a charge barrier, resulting in charge storage in the selected area. This effect was enhanced by the insertion of a  $SiO_2$  layer, which controlled the Fermi level position, between the metal layer and LN. The Al/SiO<sub>2</sub>/LN structure exhibited an energy density of  $6 \times 10^7$  C/cm<sup>2</sup> at the hole array on the LN substrate.

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# Nanowire, Nanotube and Nanoparticle Properties, Functions and Applications

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#### 1. Outline of Research

The fundamental and technological issues of using various nanomaterials, *e.g.* diverse nanowires, nanotubes and nanoparticles for the needs of structural, "green energy" and bio-medical applications have been studied using *in situ* TEM and numerous *ex situ* techniques. The objects of interest include, but are not limited to BN nanotubes and nanoparticles, CdS, Si/Ge, ZnO, ZnS and other inorganic nanowires.

#### 2. Research Activities

#### (1) Photocurrent measurements on bent CdS nanowires.

Photocurrent probing under bending of individual freestanding CdS nanowires inside HRTEM was firstly analyzed, Fig. 1.<sup>1)</sup> The experiments were conducted while carrying out 138 individual nanowire tests; this allows for the detailed statistical analysis of the photocurrent-to-dark current ratios. Although each nanowire behaves differently, from the statistical point of view, all nanostructures reveal very close photocurrent-to-dark current ratios (on/off ratios) in original, bent and recovered states, with an average value of approximately *10*, thus opening bright prospects for using CdS nanowire arrays in flexible optoelectronics.



Fig. 1. An experimental setup inside a high-resolution transmission electron microscope (HRTEM) for the comparative analyses of dark currents and photocurrents in elastically bent CdS nanowires.

# (2) Multi-functional superelastic ultralight BN nanotube cellular-network foams.

We proposed a brand-new technology for highthroughout, simple and reliable fabrication of 3D tubular cellular-architecture BN foams. For the first time, the outstanding attributes of BN nanotubes (ultrahigh Young's modulus of  $\sim 1.3$  TPa, and superb bending stress of  $\sim 260$ MPa) were smartly utilized within these novel foam-like cellular structures. The ultralight, chemically inert, cellular tubular architectures show highly porous nature, robust integrity, sustainable performance under compression (complete shape recovery even after 90% deformations), superelastic, superhydrophobic and lipophilic properties, and thermally-diffusive-stability, Fig. 2. Such impressive set of properties rivals the most optimal foam candidates known to date, such as graphene aerogels and foams, and surpasses all known superelastic 3D BN foams for using as environmental cleaners.<sup>20</sup>



Fig. 2. Ultralight BN foam made of numerous interconnected multiwalled BN nanotube skeletons; the foam possesses 98.5% porosity, superelastic properties at compression, adsorbs diverse oils from water-oil systems, and is easily recycled for the multiple usage under burning using a flame of liquidized gas spray nozzle.

# (3) Hollow BN nanospheres as B reservoir for prostate cancer treatment.

We fabricated hollow BN spheres with controlled crystallinity and B release; these result in decrease in cell viability and increase in apoptosis for prostate cancer cells. *In vivo* mice experiments by using subcutaneously injected models show that the spheres significantly suppress the prostate cancer occurrence by 75% and inhibit the tumor growth by 99.75%, which is 3 times and 143 times more effective compared to boric acid, respectively. The combination of hollow spheres with chemotherapy drug "paclitaxel" exhibits synergetic effects on the suppression of prostate tumor growth. This nanomaterial overcomes the drawbacks of presently available B agents and should function as a new agent for prostate cancer treatment.<sup>3</sup>

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# Nanosheet Electronics

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#### 1. Outline of Research

Two-dimensional (2D) nanosheets, which possess atomic or molecular thickness, have been emerging as important new materials due to their unique properties. The ultrathin thickness and high flexibility of 2D nanosheets render them appealing building blocks for constructing new electronics. Graphene is one of the most promising materials being researched today; it has many amazing functionalities such as high electron mobility and quantum Hall effects, prompting researchers to suggest that graphene will one day replace silicon in electronic devices. However, graphene is a conductor, and electronic technology also requires insulators and semiconductors. Along with graphene, 2D nanosheets have increasingly inorganic attracted fundamental research interest because of their diversity in physical properties. Among the type of 2D inorganic nanosheets, oxide nanosheets are important, fascinating research targets to be pursued because of the virtually infinite varieties of layered oxide materials with interesting functional properties. We are working on the creation of 2D oxide nanosheets and the exploration of their novel functionalities in electronic applications.

#### 2. Research Activities

#### (1) High-k Nanosheets and Their Applications.

Oxide nanosheets can be utilized as high-*k* dielectrics, which are essential for many electronic devices such as memories, capacitors, and gate insulators.<sup>1-3)</sup> For example, titania- or perovskite-based nanosheets (Ti<sub>2</sub>NbO<sub>7</sub>, (Ca,Sr)<sub>2</sub>Nb<sub>3</sub>O<sub>10</sub>) exhibit the highest permittivity ( $\varepsilon_r = 200 \sim 320$ ) ever realized in all known dielectrics in the ultrathin region (< 10 nm). We performed characterization and reliability test of nanosheet-based high-*k* capacitors. Through various *in situ* characterizations, we found that nanosheet-based multilayer capacitors afforded high capacitor density and robust thermal stability, opening a route to new capacitor devices and high temperature



Fig. 1. High temperature dielectric response of Ca<sub>2</sub>Nb<sub>3</sub>O<sub>10</sub> nanosheets.

electronics (Fig. 1). We extended our research to energystorage devices. Perovskite nanosheets exhibited outstanding energy storage capabilities, even comparable to that of Liion battery. The simultaneous improvement of energy density and thermal stability in dielectric capacitors is of critical importance, and perovskite nanosheet has great potential for a rational design and construction of new energy storage devices.



Fig. 2. Chemical design strategy for creating artificial multiferroics using oxide nanosheets.

#### (2) Multiferroic Materials from Nanosheet-Architectonics.

Multiferroic materials, in which the electronic polarization can be switched by a magnetic field, and vice versa, are of fundamental importance for new electronic technologies. However, there exist very few single-phase materials that exhibit such cross-coupling properties at room temperature, and heterostructures with a strong magnetoelectric coupling have only been made with complex techniques. Seeking to develop room-temperature multiferroics, we utilized a new chemical design for artificial multiferroic thin films using 2D oxide nanosheets as building blocks (Fig. 2).<sup>4)</sup> This approach enables engineering the interlayer coupling between the ferromagnetic and ferroelectric orders, as demonstrated by artificial superlattices composed of ferromagnetic Ti<sub>0.8</sub>Co<sub>0.2</sub>O<sub>2</sub> nanosheets and dielectric perovskite-structured Ca2Nb3O10 nanosheets. The  $(Ti_{0.8}Co_{0.2}O_2/Ca_2Nb_3O_{10}/Ti_{0.8}Co_{0.2}O_2)$ superlattices exhibited the multiferroic effects at room temperature, which can be modulated by tuning the interlayer coupling (i.e., the stacking sequence). Our technique provides a new route for tailoring artificial multiferroic materials in a highly controllable manner.

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# ZnO Core-Shell Nanowire for Optoelectronics

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#### Ken Pradel, Steven Zhang

#### 1. Outline of Research

Core-shell nanowire structures are used for optoelectronics, due to its high interfacial area, which allows for a higher electron-hole recombination.<sup>1)</sup> In this work, Zinc Oxide (ZnO) core-shell structures were fabricated.<sup>2)</sup>

#### 2. Research Activities

The process showing the fabrication of the core-shell structures is seen in Fig. 1. The AZO was first sputtered to make the seed layer and the back contact. Then, both the ZnO core and shell were fabricated using a low temperature hydrothermal method. Using this growth system, the ZnO nanowires were synthesized with either n or p-type core and an oppositely doped shell.



Fig. 1. Schematic representation of growth of core-shell nanowires.

The ZnO nanowires were then characterized by using SEM, TEM, and STEM. Fig. 2 shows the TEM and STEM images for the p-type core ZnO. In Fig. 2a, there is contrast between the core and the shell, as the core is darker in color than the shell. The reason is due to the shell has a larger thickness. Fig. 2b shows the STEM image that the voids are visible only in the core region, and there are no voids in the shell region. This shows that these voids are caused by the doping of antimony. Also, Fig. 2c shows the HRTEM image, which suggest the structure is monocrystalline due to regular lattice spacing. This is further shown in SAED pattern in Fig. 2d, as no distortion is observed despite multiple growth steps.

After characterizing the structure, the electric properties of these films were examined. For both the pn and the np samples, there is a rectification in the I-V diagrams, shown in Fig. 3a, and there is a large leakage current when the films were under reverse biased. The leakage current is caused by the random nature of nucleation and growth, which would lead to shorting, causing leakage. Then, the photoresponsitivity



Fig. 2. (a) Bright field TEM image of p-n core shell nanowire. (b) STEM image of core-shell wire. (c) HRTEM image of core-shell nanowire. (d) SAED pattern.

of the device was investigated by using a UV lamp. The UV lamp has two wavelength settings with different power level at 0.66 mW/cm<sup>2</sup> at 365 nm and 1.61 mW/cm<sup>2</sup> at 254 nm. light. From Fig. 3b, the induced photocurrent cause the conductivity to increase in both forward and reverse bias. This suggested that the photoconduction played a dominant role in the photodetecting behavior. The photoresponses were then calculated with driving voltage of 1V (reverse bias) and are 0.024 A/W and 0.015 A/W for the 365 nm and 254 nm, respectively.





In conclusion, ZnO core-shell homojunction structures were grown using a solution based hydrothermal method. By using microscopy, the signs of doping, voids caused by antimony integration, are present in the p-type ZnO. Also, the multistep growth produce single crystalline nanowires. Also, by performing optoelectronic measurements, the device could be used as a photodetector.

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# Tailored Design of Crystalline Nanoporous Materials

**Principal Investigator** 

**Yusuke YAMAUCHI** 



#### 1. Outline of Research

The research on mesoporous (nanoporous) 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. Here, we summarize our recent progress in this field.<sup>1-7)</sup>

#### 2. Research Activities

(1) A mesostructured tin phosphate (SnPi) material has been prepared in the presence of an amphiphilic block copolymer (F127), tin chloride (SnCl<sub>4</sub>), and phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) in an ethanol-water mixed solvent medium. The mesoporous SnPi material, with a large pore diameter (7.4 nm), nanocrystalline walls, a high surface area  $(310 \text{ m}^2 \text{g}^{-1})$ , and a unique flake-like particle shape, is successfully synthesized by a two-step heat treatment of the parent mesostructured SnPi under flowing N<sub>2</sub> gas followed by flowing air. Under moderate conditions (293 K and 60% relative humidity), our mesoporous SnPi shows 6.5 times more proton (H<sup>+</sup>) conductivity compared to its non-porous/ bulk analogue (SnPi-B), due to its higher surface area and unique nanocrystalline porous structure enriched with free O-H groups. The obtained crystalline structures are shown in Fig. 1.



Fig. 1. Crystalline structures in the pore walls.

(2) Hybrid organic-inorganic metal halide perovskites have fascinating electronic properties and have already been implemented in various devices. Although the behavior of bulk metal halide perovskites has been widely studied, the properties of perovskite nanocrystals are less wellunderstood because synthesizing them is still very challenging, in part because of stability. Here we demonstrate a simple and versatile method to grow monodisperse



Fig. 2. Photographs of the mesoporous silica powders after impregnation and crystallization.

CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>x</sub>I<sub>x-3</sub> perovskite nanocrystals inside mesoporous silica templates (Fig. 2). The size of the nanocrystal is governed by the pore size of the templates (3.3, 3.7, 4.2, 6.2, and 7.1 nm). In-depth structural analysis shows that the nanocrystals maintain the perovskite crystal structure, but it is slightly distorted. Quantum confinement was observed by tuning the size of the particles via the template. This approach provides an additional route to tune the optical bandgap of the nanocrystal. The level of quantum confinement was modeled taking into account the dimensions of the rod-shaped nanocrystals and their close packing inside the channels of the template. Photoluminescence measurements on CH<sub>3</sub>NH<sub>3</sub>PbBr clearly show a shift from green to blue as the pore size is decreased. Synthesizing perovskite nanostructures in templates improves their stability and enables tunable electronic properties via quantum confinement. These structures may be useful as reference materials for comparison with other perovskites, or as functional materials in all solid-state light-emitting diodes.

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# Nano-System Architectonics

**Principal Investigator** 

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#### 1. Outline of Research

The goal of Nano-System Architectonics is to create nano-systems, with novel functions, through the use of various key technologies and theories based on "nanoarchitectonics". Further, we propose to put these systems to use in such forms as next-generation information processing/communications and environmental/energy sustainability, so that they will make practical contributions to our society.

#### 2. Research Activities

We are investigating the fabrication methods and properties of single molecular wires, with the aim of realizing single-molecule devices. We have already demonstrated that two conjugated polydiacetylene (PDA) chains can be connected to a single organic molecule (phthalocyanine, Pc). This PDA-Pc-PDA system is expected to act as a molecular resonant tunneling diode. We are now investigating the properties of PDA systems, such as their electric properties or reaction properties. Recently we showed that hexagonal boron nitride (h-BN) is an ideal substrate for PDA systems, as it is both atomically flat and insulating.<sup>1,2)</sup> We found that the diacetylene polymerization rate under UV-light irradiation for the diacetylene/h-BN system was 250-320 times faster than for its diacetylene/graphite counterpart. In addition, the demonstrated polymerization pattern on h-BN indicates self-sensitization, which increases the polymerization probability of pristine diacetylene monomer molecules that are adjacent to ones that are already polymerized (Fig. 1). Both effects are attributed to the large electronic bandgap of h-BN (~ 6 eV), which allows long excited-state life times. The observed self-sensitization effect shows the energy transfer from a PDA chain to the adjacent diacetylene molecules. These findings will be important in the development of novel molecular devices.

We are also investigating fabrication methods and the new functionalities of nano-systems formed through molecular self-assembly, organization, bioand



Fig. 1. (a) Atomic force microscopy (AFM) image and (b) schematic model showing self-sensitization. (a) shows an AFM image of diacetylene molecules assembled on h-BN after UV-irradiation. The fabricated PDA chains appear as bright rectangles.



Fig. 2. (a) Transmission electron microscope (TEM) image of functionalized GO sheets. The inset shows a high-resolution TEM image of molecular nanoclusters. (b) M-H loops of functionalized GO sheets, pristine GO sheets, and pristine organometallic molecules at T = 2K. Note that the *M*-H curve of GO sheets changes linearly without hysteresis. Inset: Temperature versus coercive force  $H_c$  and remanence  $M_0$  for functionalized GO sheets.

mineralization.3-4) We recently discovered that the magnetization of graphene oxide (GO) sheets was increased by functionalization of ferrocene molecules (Fig. 2). Molecular spin is generated by ionization of the Fe ions in the molecule, which is caused by charge transfer between a molecule and a GO sheet. In their M-H loops, hysteresis, characterized by coercive force Hc and remanence M0, is clearly observed for the functionalized GO sheets. This suggests that collaborative couplings exist between molecular spins. The inset of Fig. 2b represents  $H_c$  and  $M_0$  for the functionalized GO sheets, at an onset temperature of 6 K. The small onset is partially due to small magnetic interactions between molecular spins, and partially due to the small size of the nanoclusters. The distribution of magnetic nanoclusters separately on a flat nanosheet is similar to a two-dimensional spin network and a neural network. Molecular spins or magnets on nanosheets are used as building blocks in spintronic and quantum computing devices because molecular spins work as individual logic or memory units. The mixing of the magnetic interactions with the charge transfer in the present system increases the complexity and diversity seen in studies of spin networks. Therefore, our synthetic approach to the understanding of molecular complexity and molecular spin interactions paves the way for new designs for the next-generation of information processing and communication, and for molecular quantum computation.

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# MANA Brain: Neuromorphic Atomic Switch Networks

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Adam Z. Stieg Renato Aguilera, Kelsey Scharnhorst



#### 1. Outline of Research

Transformational advances in computation are needed to address ever-increasing societal demands for the collection, processing, and analysis of large, unstructured, multisensory datasets. Through a conceptual convergence of nanoarchitectonics, neuroscience, and machine learning, we have developed hardware-adaptive neurocomputing architectures based on deeply hierarchical networks of nanoscale circuit elements.

#### 2. Research Activities

Atomic Switch Networks (ASN) seek to realize revolutionary efficiency, performance, and robustness in high-performance computing by envisioning a new approach to intrinsic computing with target applications in embedded systems, mobile devices, robotics and autonomous control. Next-generation ASN devices (1) have been used to demonstrate one of the first computational implementations (2) of pattern recognition and forecasting tasks in purposebuilt hardware without the need for pre-programming. (1) Next-generation devices.

ASN devices utilize digital measurement systems to provide spatiotemporal stimulation, monitoring and characterization in real-time. As seen in Fig. 1, ASN device comprise individual atomic switch elements embedded within a network of highly-interconnected, self-organized nanowires integrated into a CMOS compatible device platform.<sup>1)</sup> Earlier generation ASN devices have been scaled up as shown in Fig. 1 to improve real-time monitoring of device dynamics, enable multiple input data streams to be delivered to the ASN, and increase computational performance.



Fig. 1. Building next-generation devices. (Left) Schematic representation of a single atomic switch. Center: Scanning electron microscope image of an ASN device comprising individual atomic switch elements embedded within a network of highly interconnected silver wires. (Right) Self-organized nanowires integrated into a CMOS-compatible device platform with 120 electrodes.

#### (2) Computational Tasks.

Efforts to develop radically new computing paradigms have intensified in recent years, where the technological promise of computation beyond the digital realm for cheaper, faster, more robust, and more energy-efficient information processing. ASN devices utilize the intrinsic memory capacity and adaptive interactions of functional nanoscale elements, namely atomic switches, to generate a class of emergent operational characteristics reminiscent of natural systems<sup>2)</sup> which can be readily applied to real-time information processing and computational tasks, specifically in the area of Reservoir Computing (RC).<sup>3)</sup> To harness the dynamical response of ASNs for real-time computation, we have implemented a series of benchmark RC tasks in experiment and simulation geared toward applications in pattern recognition, object tracking, autonomous control and trend prediction from time-varying input data as shown in Fig. 2.



Fig. 2. RC using ASN devices. (Top) The nonlinear dynamics of ASN devices provides a capacity transform input information into multiple signals simultaneously acquired at readout nodes. These nodes form a linear output layer which undergoes training to effectively produce the target signal for the Parity-N test by combining the transformed output signals. (Bottom) The time series prediction task uses a subset of data to "train" a model which can be used to predict future values (top).

A contextual pattern classification/recognition task known as Parity-N, which requires both fading memory and an ability to integrate information from different points in time, has been successfully implemented with efficiencies as high as 78%. A forecasting task known as chaotic time series prediction, which requires a capacity to make short-term predictions of the future behavior of a time series using information based only on past values, was successfully implemented in both simulation and experiment with performance efficiencies of up to 80% and 95.3%, respectively.

By successfully implementing a series of real-time computational tasks, ASN devices have realized their potential utility for information processing and computing applications. These results support the viability of ASNbased and related nanoarchitectures to address the growing need for energy-efficient, adaptive computing systems which can be integrated with modern information and communication technologies.

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# **Exploring Topological Phenomena and Functionality**

#### **Principal Investigator**

MANA Scientist MANA Research Associate NIMS Postdoctoral Scientist Graduate Student Xiao HU Toshikaze Kariyado Takuto Kawakami Hong-Xing Yang Zhao Huang, Long-Hua Wu



#### 1. Outline of Research

The Nobel Prize in Physics of 2016 was awarded to Thouless, Haldane and Kosterlitz for their pioneering theories on topological phase transition and topological phase of matter. The discovery of quantum Hall effect (QHE) of two-dimensional (2D) electron gas under strong perpendicular magnetic field by von Klitzing opened a new chapter in condensed matter physics. Thouless revealed that the integer coefficient in Hall conductance is given by the Chern number associated with topological phase of electronic wave functions at Landau levels. Afterword, Haldane discovered that nontrivial topology can be created by electronic states with finite Berry curvature defined in momentum space on Bloch electronic wave functions even without external magnetic field. Similar to QHE, the quantum anomalous Hall insulator supports dissipationless edge current. Since then to explore possible topological states in terms properties inherent in materials, such as spinorbit coupling and/or magnetism has been one of the main driving forces in study of condensed matter physics and related materials science.1)

The concept of topology fostered in electronic systems has been extended to a wealth of systems, and topological superconducting and electromagnetic states have also been explored. It is revealed theoretically that in a topological superconductor, zero-energy quasiparticle excitations known as Majorana bound states (MBS) obey non Abelian statistics and can be used for implementing decoherencefree quantum computation. In topological photonic crystals, a unidirectional propagation of electromagnetic wave can be achieved at the sample edge. In terms of an approach coined "topological nanoarchitectonics", we have been exploring novel topological phenomena and quantum functionality derived from topology.

#### 2. Research Activities

#### (1) Helical spin structure of Majorana bound state.<sup>2)</sup>

A topological superconducting state can be created in a heterostructure of a s-wave superconductor and a quantum spin Hall insulator (QSHI), as shown schematically in Fig. 1a. When a ferromagnetic insulator (MI) is laid covering a part of the edge of QSHI, a zero-energy MBS is induced. Solving the Bogoliubov-de Gennes equation, we found that there is a helical spin texture in the MBS wave function with a pitch proportional to the Fermi momentum (Fig. 1b). This spin texture can be observed by magnetooptic techniques, which serves as a verification of MBS.

When the sepration between two MI matches the wave length of the helical spin structure, two MBS take exactly zero energy, which corresponds to a constructive interference between the two MBS. Rotating magnetiza- tion in one of



Fig. 1. (a) Schematic of the heterostructure of a 2D QSHI and a s-wave superconductor where two MBS are induced by two MI; (b) helical spin texture formed by the interference of MBS; (c) and (d) DOS of quasiparticle excitations as function of relative direction of magnetizations in MI close to MI and at the center point between MI respectively.

the two MI will then drive MBS from zero energy. Because of the absence of any quasiparticle excitations within the superconducting gap, the system can still be described by the bonding and anti-bonding states of MBS, which carry a fermionic character associated with the even- and oddnumber of electrons in the system, as shown by the blue and green curves in Figs. 1c and 1d. The oscillation of the density of states of quasiparticle excitations exhibits a  $4\pi$  period of the direction of magnetization, which can be clearly seen in DOS at the center point between the two MI, where a discontinuous jump appears between the two parity states.

#### (2) A new topological state on honeycomb lattice.<sup>3)</sup>

We have formulated a new way to generate nontrivial topology in tight-binding model defined on honeycomb lattice for spinless electrons with nearest-neighbor hopping. When all sites of honeycomb lattice are grouped into hexagons, and the hopping integral between hexagons is tuned stronger than that inside hexagons, the system is driven into a topological state. The topological phase transition is signaled by a gap opening at the Dirac cone achieved in the system of uniform hopping energy, and is accompanied by a band inversion at  $\Gamma$  point of BZ between p and d orbits accommodated on the hexagons. The orbital angular momenta of the p and d orbits play the role of pseudo spin, which are intimately related with the 2D presentations of the  $C_{6v}$  point group. The topological energy gap is given by the difference between the intra- and interhexagon hopping integrals, which opens a new route towards robust topological states.

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# Surface Atomic Scale Logic Gate and Mechanics

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C. Durand, G. Dridi, O. Faizy-Namarvar W.H. Soe, D. Sordes



#### 1. Outline of Research

The Pico-Lab CEMES-CNRS Toulouse MANA satellite is working on the experimental and theory of QHC logic gates design, current intensity drive and mechanical inputs. It is exploring atomic scale logic gate complexity to master the emergence of quantum computing power inside a single molecule or at the surface of a passivated semi-conductor.

#### 2. Research Activities

(1) Running the LT-UHV – 4 STM/NC-AFM & UHV SEM.

The LT-UHV 4-STM was used on an Si(100)H 2x1 surface (intrinsic silicon sample) to precisely localized the dimer rows at -V (apparent ½ shift of the STM image row at +V)<sup>1)</sup> and record a single tip atom contact on a single surface H atom in preparation of a single DB atomic wire contact. During each single tip approach, tunnel, van der Waals, mechanical and chemical contacts were successively observed reaching a very low G=0.000001 Go contact conductance. Bulk and surface band bending's are causing this very low G raising questions on how to contact with an atomic precision a surface a single atomic scale DB wire without deforming its designed electronic structure.

#### (2) Design of complex QHC logic gates.

Per logical output, a QHC gate design relies on the quantum transduction of its Heisenberg-Rabi (H-R) oscillations in a tunneling current intensity (Fig. 1). It is essential to optimized this transduction performed in QHC by two metallic nano-pads per output<sup>2)</sup> where  $|\Phi_a>$  and  $|\Phi_b>$  in Fig. 1 are in electronic interactions with those pads. We have demonstrated that  $|\Phi_a>$  and  $|\Phi_b>$  are the two pointer states of this transduction process<sup>2)</sup> and that the T(E<sub>f</sub>) electronic transmission used in the Landauer formula is the result at the Fermi energy of a filtering quantum transduction.<sup>2)</sup>

with  $C_b(t) = \langle \Phi_b | \Psi(t) \rangle$  the  $|\Phi_b \rangle$  H-R amplitude on  $|\Psi(t) \rangle$  (initial meas. prep.  $|\Phi_a \rangle$ ) and  $|\Psi(t) \rangle$  the time dependent quantum state describing the QHC measurement per output.

#### (3) Single molecule latch for QHC binary data input.

For inputting binary data on a QHC dangling bond circuit on an Si(100)H surface, elongated arm moleculelatches were explored, acetophenone-like molecule-latches synthesized and molecules chemisorbed on Si(100) 2x1 in a very sub-monolayer coverage.<sup>3)</sup> The reversible flip-flop like vertical motion of this molecule-latch was observed, triggered by an STM tunneling current while positioning the tip apex at the vertical of the latching pivot.<sup>3)</sup> Fig. 2 is presenting the 4-acetylalkylphenyl next generation of molecule latches.

#### (4) Mechanics.

This year was the preparation of the 1<sup>st</sup> International Nanocar race in spring 2017 at Toulouse MANA satellite. The LT-UHV 4-STM was transformed in a 4 independent ultra-stable LT-UHV-STM on the same surface for driving 4 different molecule-vehicles. Five of the sixth registered teams beneficiated of 2 weeks long training sessions.<sup>4)</sup> The MANA-NIMS team Bis-binaphthyl-durene (BBD) double paddle vehicle was studied leading to the understanding on how to manipulate mechanically BBD for reaching a fully planar conformation on Au(111) to free its front and rear molecular paddles ready for the race (Fig. 3).

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Fig. 1. (1) the tunnel jonction and (2) its TB model used to measure the logical output of a QHC logic gate. Here, the QHC gate is a simple universal 3 states system with its |Φ<sub>b</sub>> reading block states. The classical to quantum (C/Q) & quantum to classical (Q/C) transductions are performed by the 2 metallic nano-pads in grey.



Fig. 2. Calculated switching path of a 4-acetylalkylphenyl moleculelatch (a) mounted as presented in (b) on an atomic scale interferometer circuit designed on a Si(100)H surface.



Fig. 3. (a) Constant current image (2 nm x 1.2 nm, 0.1 V, 10 pA) of a BBD molecule (b) with one STM of the LT-UHV 4-STM. (c) The extracted surface conformation after a specific STM manipulation protocol to reach this planar BBD configuration on Au(111).

### Analysis of K<sub>x</sub>Fe<sub>2-y</sub>Se<sub>2</sub> Superconductor with Nano-scale Phase Separation Principal Investigator Yoshihiko TAKANO

MANA Scientist MANA Research Associate **Yoshihiko TAKANO** Hiroyuki Takeya Masashi Tanaka



#### 1. Outline of Research

Iron-based superconductors are expected to be candidate materials for superconducting device under high magnetic field. Layer structured iron selenide, FeSe is one of the iron-based superconductor and has the simplest crystal structures among them. It shows superconductivity with transition temperature ( $T_c$ ) around ~10 K. It has been reported that the  $T_c$  was enhanced up to ~37 K under high pressure. Even a  $T_c$  ~44 K has also been observed in ultrathin FeSe films. These facts imply that the  $T_c$  can be improved by the nano-scale tuning of crystal lattice.

Potassium insersion in between FeSe layers also enhances the  $T_c$  to ~44 K. However, the potassium intercalated FeSe,  $K_xFe_{2,y}Se_2$ , shows an intrinsic nano-scale phase separation into superconducting  $K_xFe_2Se_2$  (122-) phase and insulating  $K_2Fe_4Se_5$  (245-) phase. Then, the relationship among the surface morphology, compositional ratio and crystal structure has not yet been clarified. In our research, the growth mechanism and superconducting properties of single crystalline  $K_xFe_{2,y}Se_2$  have been investigated.



Fig. 1. Temperature dependences of (a) magnetization and (b) resistivity of quenched or slow-cooled single crystals. Quenched crystals show a large diamagnetic signal, and a sharp superconducting transition around 30 K. On the other hand, slow-cooled one show surprisingly high  $T_c$  onset of ~44 K, even though the shielding fraction is small.

#### 2. Research Activities

Single crystals of  $K_xFe_{2,y}Se_2$  were prepared by a "onestep method" with quenching at various temperatures. The superconducting properties and surface morphology were strongly affected by the quenching temperature. And it was found that slow-cooling treatment process realizes a  $T_c$  of ~44 K (Fig. 1), with a creation of island-like morphology on the surface of single crystals.

*In-situ* high-temperature single crystal X-ray diffraction measurements provide us a hint as to how to generate such a higher  $T_c$  phase, suggesting that the insulating 245 phase structure was found<sup>1</sup> to be grown below 280°C (Fig. 2).

TEM measurements supported by a micro-sampling technique directly revealed that the island-like parts



Fig. 2. Schematic illustrations of unit cells for (a) the 122-phase, K<sub>x</sub>Fe<sub>2</sub>Se<sub>2</sub>, and (b) the Fe-vacancy ordered 245-phase, K<sub>2</sub>Fe<sub>4</sub>Se<sub>5</sub> (K<sub>0.8</sub>Fe<sub>1.6</sub>Se<sub>2</sub>), structures. (c), (d) The corresponding FeSe lattice viewing along c-axis direction. Single crystal X-ray diffraction spots in the *hkθ* section at room temperature (e), and 280 °C (f).

correspond to the K<sub>x</sub>Fe<sub>2</sub>Se<sub>2</sub> structure having a perfect FeSe layers as shown in Fig. 3. The appearance of higher  $T_c$  onset of 44 K is attributed to the formation of 122-phase with perfect FeSe layers assisted by the growth of 245-phase.<sup>2</sup> Our findings revealed the origin of  $T_c \sim$ 44 K in K<sub>x</sub>Fe<sub>2-y</sub>Se<sub>2</sub> single crystals.



Fig. 3. Procedures of the microsampling technique. The microsamples are thinned down to 40-100 nm in both orientations after attaching to the TEM carrier. EDX elemental mapping were carried out in the *ab*-plane of the fabricated microsamples. Electron diffraction patterns on the island-like part shows clear diffraction spots identical to those of the 122-phase crystal structure.

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# Atomic Switches and Related Nanoionic Devices

MANA Principal Investigator MANA Scientist MANA Research Associate Kazuya TERABE Tohru Tsuruoka, Takashi Tsuchiya Karthik Krishnan



#### 1. Outline of Research

Not only fabrication scale for the conventional semiconductor devices, but also the physical operating is being reached limit in near future. To continue upgrading information and communication devices, it is essential to create next generation nanodevices operating under new principles. A promising type of such nanodevices is the nanoionics device, which is operated by controlling the local ion migration and electrochemical reaction instead of electron and hole migration. Our group has been focusing to develop novel nanoionic devices with unique functions.<sup>1)</sup> Recently, a polymer-based quantized conductance atomic switch and a magnetic property tunable nanoionic device have been successfully developed.

#### 2. Research Activities

# (1) Development of a polymer-based quantized conductance atomic switch.<sup>2)</sup>

We have observe quantized conductance in an atomic switch device consisting of a 40-nm thick polyethylene oxide (PEO) film sandwiched between electrochemically active Ag and inert Pt electrodes at room temperature under atmospheric conditions. Under sweeping of a bias voltage, multiple inters of  $G_0$  (=2 $e^2/h$ , where *e* is the charge of the electron and h is Planck's constant) were observed with half-integers and fractional conductance variations, as shown in Fig. 1(a,b). Highly reproducible quantized conductance is achieved by optimizing the device structure and the measurement conditions, such as the maximum applied voltage and the voltage sweep rate. First-principles density functional theory simulations suggest the importance of structural relaxation of the atomic point contact in determining the quantized conductance state (Fig. 1(c,d)). These findings will contribute to the development of new multilevel memories, quantum information processing, and neuromorphic systems.

# (2) Development of a magnetic property tunable nanoionic device.<sup>3)</sup>

We have observed *in situ* tuning of magnetic property in a Fe<sub>3</sub>O<sub>4</sub> based all-solid-state nanoionic device shown in Fig. 2(a). The device operates on the basis of magnetic property modulation in the Fe<sub>3</sub>O<sub>4</sub> thin film due to Li<sup>+</sup> ion insertion and removal and the resultant electronic carrier density modulation. Fig. 2(b) shows normalized M (magnetization)-H(magnetic field) loops measured at various DC voltage. Typical ferromagnetic hysteresis of Fe<sub>3</sub>O<sub>4</sub> was observed for all voltage conditions. The device exhibited a gradual decrease in M above 10 kOe with an increasing positive



Fig. 1. Quantized conductance behavior observed in an Ag/PEO/Pt atomic switch (a) and typical conductance-state histogram (b). Energy-dependent conductance (c) and eigenstates with different eigenvalues for a specific point (indicated by the arrow) calculated by first-principles density functional theory (d).

voltage to LCO, *i.e.*, Li<sup>+</sup> insertion into Fe<sub>3</sub>O<sub>4</sub>. The normalized M was tuned from unity to 0.64 at 2 V, and the variation from 0 to 2 V was repeatable (not shown), indicating that the M tuning in the voltage region was due to reversible Li<sup>+</sup> insertion and removal. The decrease in M achieved with the present technique can be applied to high-density magnetic storage devices. Furthermore, it offers promising advantages for spintronics application because the electron donation gains spin polarization of Fe<sub>3</sub>O<sub>4</sub> thin film, resulting in enhanced magnetoresistance effect.



Fig. 2. Schematic illustration of all-solid-state redox transistor with Fe<sub>3</sub>O<sub>4</sub> and Li<sub>4</sub>SiO<sub>4</sub> lithium ion conductor (a). Li<sup>+</sup> represents positively charged lithium ions. Dotted circles in LiCoO<sub>2</sub> represent Li<sup>+</sup> vacancies. *M*-*H* loops of device measured at various DC voltages (b).

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#### Self-Limiting Oxides on WSe<sub>2</sub> as Controlled Surface Acceptors and Low-Barrier Hole Contacts Principal Investigator MANA Research Associate Kazuhito TSUKAGOSHI Mahito Yamamoto



#### 1. Outline of Research

Growing a high-quality oxide film with a tunable thickness on atomically thin transition metal dichalcogenides is of great importance for the electronic and optoelectronic applications.<sup>1)</sup> We developed balnd-new thin film transistor with precisely controlled stacking atomic film using the transition metal oxides.<sup>2)</sup>

#### 2. Research Activities

We have developed that ozone (O<sub>3</sub>) exposure leads to homogeneous surface oxidation of atomically thin  $WSe_2$ with a self-limiting thickness from single- to trilayers, depending on temperature. The atomically thin films of under-stoichiometric tungsten oxides (WO<sub>x</sub> with x < 3) grown on tungsten diselenide (WSe<sub>2</sub>) can be used as both controlled charge transfer dopants and low-barrier contacts for p-type WSe<sub>2</sub> transistors (Fig.1).



Fig. 1. (a) Schematics of a bilayer WSe<sub>2</sub> transistor before and after O<sub>3</sub> exposure at 100 °C for 1 h. (b) AFM image of a bilayer WSe<sub>2</sub> transistor after O<sub>3</sub> exposure at 100 °C for 1 h. The scale bar is 2 μm. The inset is the optical microscope image.

Exposure of atomically thin WSe<sub>2</sub> transistors to ozone (O<sub>3</sub>) at 100 °C results in self-limiting oxidation of the WSe<sub>2</sub> surfaces to conducting WO<sub>x</sub> films (Fig. 2). The WOx-covered WSe<sub>2</sub> is highly hole-doped due to the surface electron transfer from the underlying WSe<sub>2</sub> to the high electron affinity WO<sub>x</sub>. The dopant concentration can be reduced by suppressing the electron affinity of WO<sub>x</sub> by air exposure, but exposure to O<sub>3</sub> at room temperature leads to the recovery of the electron affinity. Hence, the surface transfer doping with WO<sub>x</sub> is virtually controllable (Fig. 3).

Transistors based on WSe<sub>2</sub> covered with WO<sub>x</sub> show only p-type conductions with orders of magnitude better oncurrent, on-off current ratio, and carrier mobility than without WO<sub>x</sub>, suggesting that the surface WO<sub>x</sub> serves as a p-type contact with a low hole Schottky barrier. Our findings point to a simple and effective strategy for creating p-type



Fig. 2. (a) Id-Vg characteristics of a bilayer WSe<sub>2</sub> transistor before (black line) and after (red line) O<sub>3</sub> exposure at 100 °C for 1 h (Vd = 1 V). (b) Id-Vd characteristics of the oxidized bilayer WSe<sub>2</sub> transistor with Vg ranging from -40 to 40 V.



Fig. 3. (a) Id-Vg characteristics of a WOx-covered single-layer WSe<sub>2</sub> transistor upon intermittent air exposure from 0 to 10 h. (b) Id-Vg characteristics of the transistor after 10 h of air exposure, followed by intermittent O<sub>3</sub> exposure from 0 to 60 min at room temperature. The drain bias is 10 mV. The arrows in (a,b) indicate the evolution of exposure time. (c) Time evolution of Id upon exposure to air (black square dots) and O<sub>3</sub> (red circular dots) at Vd = 10 mV and Vg = 0 V. The black and red solid curves are exponential and allometric fits, respectively. (d) Changes in Id upon the cyclic exposure of air for 20 min (black square dots) and O<sub>3</sub> for 10 min (red circular dots) at Vd = 1 V and Vg = 0 V.

devices based on two-dimensional transition metal dichalcogenides with controlled dopant concentrations.

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# Nanoarchitectonics of Hybrid Artificial Photosynthetic

### System

MANA Principal Investigator (Field Coordinator)

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Huimin Liu, Huabin Zhang, Xianguang Meng Guigao Liu, Mu Li, Qing Yu, Li Shi



#### 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.



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

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

#### 2. Research Activities

 Efficient Visible-Light-Driven Carbon Dioxide Reduction by a Single-Atom Implanted Metal–Organic Framework.<sup>19</sup> Modular optimization of metal–organic frameworks (MOFs) was realized by incorporation of coordinatively unsaturated single atoms in a MOF matrix. The newly developed MOF can selectively capture and photoreduce CO<sub>2</sub> with high efficiency under visible-light irradiation. Mechanistic investigation reveals that the presence of single Co atoms in the MOF can greatly boost the electron-hole separation efficiency in porphyrin units. Directional migration of photogenerated excitons from porphyrin to catalytic Co centers was witnessed, thereby achieving supply of long-lived electrons for the reduction of CO<sub>2</sub> molecules adsorbed on Co centers. As a direct result, porphyrin MOF comprising atomically dispersed catalytic centers exhibits significantly enhanced photocatalytic conversion of CO<sub>2</sub>, which is equivalent to a 3.13-fold improvement in CO evolution rate and a 5.93-fold enhancement in  $CH_4$  generation rate compared to the parent MOF (Fig. 2).



Fig. 2. Left: Production yield of CO and CH<sub>4</sub> over MOF-525-Co photocatalyst. Right: Schematic illustration of photocatalytic CO<sub>2</sub> reduction over the single atom implanted MOF matrix.

(2) PdAu alloy plasmonic nanoparticles for efficient  $CO_2$ reforming with methane under visible light irradiation.<sup>2)</sup> Photo-catalytically reducing CO<sub>2</sub> with methane (CRM) into syngas is beneficial for both relieving the fossil fuel crisis and protecting the environment. Here, the alloys between a group 8 metal and a group 11 element, PdAu alloys in this case, were firstly developed as catalysts. By increasing the content of Au in the Pd<sub>x</sub>Au<sub>y</sub> alloys, the electronic structure of Pd could be gradually tuned to electron deficient, which favored the stability of the Pd<sub>x</sub>Au<sub>y</sub>/ Al<sub>2</sub>O<sub>3</sub> catalysts in CRM. Meanwhile, the plasmonic absorption in visible light region and the electromagnetic field induced by hot electrons were enhanced in Aucontaining Pd<sub>x</sub>Au<sub>y</sub> alloys, which facilitated CO<sub>2</sub> activation and was regarded to be responsible for accelerating the reaction rate with visible light irradiation. This study provides promising approach for applying alloys in photodriven or photo-assisted reaction systems.

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# **Development of Thermal Energy Materials**

**Principal Investigator** 

Takao MORI



#### 1. Outline of Research

Approximately two thirds of primary energy (fossil fuels, etc.) being consumed in the world, sadly turns out to be unutilized, with much of the waste being heat. It is imperative to develop better thermal management (insulators, thermal dissipation, etc.) materials. The direct conversion of waste heat to electricity is also a large incentive to find viable thermoelectric (TE) materials.<sup>1)</sup> Traditionally, high performance TE materials have tended to not be element friendly; being composed of Bi, Te, Pb, etc. In order to functionalize abundant and safe elements, novel concepts & materials need to be developed.<sup>2-4)</sup>

#### 2. Research Activities

#### (1) Novel concepts for TE enhancement.

1A. Nano-micro pores for high ZT. Porous materials have typically yielded low thermoelectric performance because the decrease in thermal conductivity usually cannot make up for the loss of electrical conductivity. We have utilized phase diagrams to create a second phase in the champion mid-high temperature skutterudite material, which could be annealed to result in well-distributed nanomicro pores. As a result of our design, excellent phonon selective scattering was achieved, to yield a 100% enhancement of the figure of merit ZT, an unprecedented  $ZT\sim1.6$  for rare earth-free skutterudites (Fig. 1).<sup>5)</sup> This material has several advantages for applications beyond being rare earth-free. Namely, unlike typical nanostructured materials, stability of ZT under temperature, and improved oxidation resistance.<sup>5)</sup>

*1B. Hybrid effect.* The simultaneous enhancement of electrical conductivity and Seebeck coefficient observed in a nanocomposite was attributed to a hybrid effect based on a partly percolating conductive network.<sup>60</sup> Interface and size effects are considered to also possibly play a role.

*1C. Magnetic systems.* We recently clarified the importance of the interaction of the charge carrier and magnons.<sup>4)</sup> Several magnetic systems were further investigated,<sup>7)</sup> and relatively high *ZT* obtained.<sup>8)</sup>



Fig. 1. Image of porosity creation and high *ZT* realized for RE-free empty skutterudites.<sup>5)</sup>



From material design, layered complex metal nitrides

AMN<sub>2</sub> are gathering interest.<sup>9)</sup> Several new systems showed the wide tunability of this materials class.<sup>10)</sup> A home-made CVD was constructed and yielded fast growth of SrB<sub>6</sub> boride films with large Seebeck coefficients.<sup>11)</sup>



Fig. 2. Zr-doping sites in β-B and Seebeck coefficients.<sup>13)</sup>

(3) Development of high temperature TE materials for topping cycles in thermal power plants.

Applications for high temperature TE materials including power plant topping was reviewed.<sup>12)</sup> Advancements have been made in the thermoelectric borides which are promising candidates.

3A. Excellent p, n control. Lack of n-type higher borides have been a problem for applications. Through strategic doping of void sites in elemental  $\beta$ -rhomobohedral boron, excellent control of p-n characteristics (400  $\mu$ VK<sup>-1</sup> to -650  $\mu$ VK<sup>-1</sup>) was achieved (Fig. 2) in a system with the same crystal structure and consisting of the same elements.<sup>13)</sup>

3B. Origin of enhancement in  $SmB_{66}$ . 40 times ZT enhancement compared to the Y phase was observed for the Sm phase in the  $RB_{66}$  system. YbB<sub>66</sub> was also discovered to exhibit similar enhancement. Relatively large electronic specific heat term (relatively heavy carrier mass) was indicated to be a possible origin.<sup>2)</sup> Investigations into the valency of Sm were also carried out at SPRing8.

(4) Development of thermal insulation materials.

Synthesis of aerogel thermal insulation materials with thermal conductivity smaller than air were improved in an industry-friendly method.<sup>14</sup>

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# Solid-State Batteries

Principal Investigator MANA Scientist MANA Research Associate Kazunori TAKADA Tsuyoshi Ohnishi Koichi Okada



#### 1. Outline of Research

Lithium-ion batteries have been powering portable electronics including cellular phones and note PC's for more than 20 years. In addition, they are expected to play new roles for realizing a low-carbon society as power sources in electric vehicles and energy storage devices in smart grids. However, there are still some issues to be solved. Because part of the issues arise from the organic electrolytes used in the batteries, they are expected to be solved in solid-state batteries.

#### 2. Research Activities

(1) Orientation alignment of epitaxial LiCoO<sub>2</sub> epitaxial films.<sup>1)</sup>

Battery performance is governed not only by bulk properties of the battery components but also by their interfaces, and the latter is often rate determining especially after the development of highly ion-conducting solids. However, studies on the interfacial ionic conduction are still in their infant stage. One of the reasons is the lack of ideal interfaces available for fundamental studies, and epitaxial growth is regarded as a promising way to the ideal interfaces.

LiCoO<sub>2</sub>, which is a typical cathode material in lithium batteries, grows on SrTiO<sub>3</sub> (100), (110), and (111) epitaxially with (104), (018), and (001) orientations, respectively. The interlayers are most upright and thus accessible for lithium ions in the (104) orientation, which is the most appropriate for the studies on interfaces. However, the (104) film exhibits four-domain structure, in which domain boundaries exist and may influence the transport phenomena and lead to non-ideality at the interfaces. Because LiCoO<sub>2</sub> grows with its *c*-axis parallel to four equivalent <111> directions of SrTiO<sub>3</sub> (100) substrates to exhibit the four-domain structure,



Fig. 1. Azimuthal phi scans of  $LiCoO_2\ 003$  reflections for the epitaxial films grown on  $SrTiO_3$  substrates.

vicinal surface breaking the equivalency is employed in order to induce preferential growth of specific orientation in this study. In addition, increasing off-cut angle and lowering deposition rate to facilitate step-flow growth mode aligns the *c*-axes into one <111> direction completely, as shown in Fig. 1.

# (2) Improved cycling performance of silicon anodes in solid-state systems.<sup>2)</sup>

Lithium–silicon alloys are regarded as anode materials with the greatest potential because of the high theoretical capacity more than ten times higher than that of graphite, low electrode potential, and high abundance. However, they exhibit huge volume change upon the charge/discharge cycling, which results in low power density and rapid capacity fading. Our previous studies have revealed that the disadvantages are improved in solid electrolytes; however, the cycling performance is not satisfactory for practical use.

It has been reported that cycling performance of alloy anodes is improved in convertible oxides, which produce alloyable metal nanoparticles stabilized in inactive scaffolds by conversion reaction. However, introduction of oxygen decreases the capacity. This study demonstrates that even a small amount of oxygen effectively improves the cycling performance in solid electrolyte systems. The SiO<sub>0.4</sub> film in Fig. 2 prepared by reactive sputtering shows little capacity fading over the 100 cycles. It delivers a high capacity close to 3000 mAh g<sup>-1</sup> owing to the low oxygen content.



Fig. 2. Cycling performance of *a*-Si films in a solid electrolyte. The open and filled circles indicate the charging and discharging capacities, respectively.

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# Nano-System Computational Science

**Principal Investigator** 

#### Yoshitaka TATEYAMA



#### 1. Outline of Research

We are challenging to make novel theoretical frameworks for physicochemical phenomena such as electron transfer, proton transfer & photoexcitation (Fig. 1), and the corresponding efficient computational techniques for highperformance computing.

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 rare event sampling, and (2) understanding microscopic mechanisms of elementary reactions in physical chemistry problems by applying these computational techniques. Of particular interest is surface/ interface electrochemistry in catalysis, solar cell and Li-ion battery.



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

#### 2. Research Activities

Regarding the solar cells, we carried out DFT analyses of interfacial properties of dye-sensitized solar cell  $(DSC)^{1}$ and perovskite solar cell (PSC).<sup>2)</sup> For the former, cosensitization mechanisms between N3 and squaraine dyes are theoretically examined. We found that N3/HSQ1 cosensitization improves the IPCE due to a steric repulsion between the dyes, reducing the quenching by the electron transfer (Fig. 2). The results suggest that the competition between the quenching and the dye regeneration is a key to determine the efficiency of the cosensitization.



Fig. 2. A schematic picture of the mechanisms of N3/HSQ1 and N3/ SQ1 cosensitizations.

In the field of catalysis we focused on understanding the interaction of solid liquid interfaces in particular the interaction of water with cerium oxide supported platinum clusters by the means of ab initio molecular dynamics calculations.<sup>3)</sup>

We revealed that at the water/ceria interface the water molecules undergo spontaneous dissociation until an equilibrium concentration of surface OH groups is reached. These dissociated molecules then facilitate proton hopping between the water molecules and the adsorbed OH groups similar to the Grotthus mechanism. This mechanism allows for transfer of the protons and OH groups over long distances on the ceria surface, which then has impact on water interactions with metal clusters (Fig. 3). OH groups originating from water molecules dissociated at water ceria interface are driven and transported via the proton diffusion mechanism towards the Pt cluster, where the OH adsorption results in charge transfer from the Pt cluster to the ceria support reducing additional Ce ion.



Fig. 3. A schematic picture of OH transfer over long distance on  $CeO_2$  surface, resulting in OH adsorption on ceria supported Pt cluster.

On the battery researches, we investigated LiO<sub>2</sub> states in several electrolyte solutions for understanding discharging processes of Li-O<sub>2</sub> battery.<sup>4)</sup> In addition, we elucidated the effects of the FEC additives and the LiF formation on the properties of solid electrolyte interphase (SEI) films.<sup>5)</sup>

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### Construction of Interphases with Atomic/Molecular Order for Efficient Conversion of Energy and Materials Principal Investigator Kohei UOSAKI

MANA Research Associate Graduate Student Hung Cuong Dinh, Shuo Yang Huiwen Lin



#### 1. Outline of Research

One of the most challenging tasks for chemists/ material scientists is the construction of efficient conversion systems of energy and materials. In particular, development of highly efficient electrocatalysts is the key to achieve sustainable society because of their central roles in interfacial energy conversion such as water electrolysis to generate hydrogen and fuel cell. Pt group metals (PGMs) and their alloys are known to be one of the most efficient electrocatalysts but due to the high cost, less abundance, and still sluggish kinetics, we need to find novel electrocatalysts. To establish structure-function relations and to rationally design and construct the desired interfacial phases, chara- cterrization of the structure and functions of the interfaces in situ and theoretical studies must be carried out.

#### 2. Research Activities

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

We have already demonstrated that overpotential for methanol oxidation could be reduced by using twodimensionally ordered Pt-Ru nanocomposites prepared by arranging Pt-Ru multinuclear complexes followed by heat treatment.<sup>1)</sup> This year we extended this method to Pt-Ni so that amount of precious metal can be reduced.<sup>2)</sup>

Nitrogen doped carbon nanostructures are known to have effective metal free oxygen reduction reaction (ORR) catalyst, although the activity is still limited. We developed various methods to obtain C, N architectures with high activities for both ORR and hydrogen evolution reaction (HER).<sup>3,4)</sup> We have predicted theoretically<sup>5)</sup> and proved experimentally<sup>6,7)</sup> that BN nanosheet (BNNS) on Au electrode is an effective ORR catalyst, although, the overpotential is still high and oxygen is reduced to  $H_2O_2$  by 2-electron process while it is reduced to H<sub>2</sub>O by 4-electron process at Pt. This year we found that deco- ration of BNNS with gold nanoparticles not only reduces the overpotential for ORR further by ca. 50 mV but also opens a 4-electron reduction route to water (more than 50 % of oxygen is reduced to H<sub>2</sub>O. Theoretical analysis of free energy profiles for ORR at the BN monolayer shows that significant stabilization of adsorbed oxygen atom by the Au cluster makes 4-electron reduction possible.

Considering high hydrogen adsorption/storage ability of BN, electrocatalytic activity for HER is also examined. Fig. 1 shows overpotential at Au electrode is reduced significantly by the BN modification. The smaller the BNNS sizes, the higher the HER efficiency. The overpotential at BNNS (0.1–0.22  $\mu$ m)/Au is only 30 mV larger than that at Pt electrode. Theoretical calculation shows that the origin of small overpotential is due to the energetically favored sites for intermediate state of HER, adsorbed hydrogen.<sup>8)</sup>



Fig.1. Current – potential relations at (i) bare Au, (ii) BNNS (unfilterated)/ Au, (iii) BNNS (0.45-1.0  $\mu$ m)/Au, (iv) BNNS (0.22-0.45  $\mu$ m)/Au, (v) BNNS (0.1-0.22  $\mu$ m)/Au and (vi) bare Pt in Ar saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> solution. Scan rate: 1 mV/s. Inset: Size distribution of the BNNS.

#### (2) Investigations of Structure and Electron Transfer Processes at Solid/liquid Interfaces.

In order to understand mechanism and improved the efficiency of interfacial energy conversion processes, it is essential to have information of geometric, electronic, and molecular structures of the interfaces in situ in real time.<sup>9)</sup>

We have shown that metal complexes on and within molecular layers formed on Si(111) electrode surface act as "confined molecular catalyst" for photoelectrochemical HER<sup>10a)</sup> and CO<sub>2</sub> reduction.<sup>10b)</sup> We have proved by XPS and XAFS that Pt complexes are incorporated into the molecular layers and act as confined molecular catalysts for both HER and CO<sub>2</sub> reduction without being converted into metallic Pt.<sup>11)</sup> Time-resolved spectroelectrochemical study shows that electron is transferred from Si to proton via viologen moiety and the Pt complex.<sup>12)</sup>

Potential-dependent structures of the Pt(111) electrode in perchloric and sulfuric acid solutions were characterized by surface x-ray scattering  $(SXS)^{13}$  and interfacial structures of lithiated Si(111) were studied by SXS and soft x-ray emission spectroscopy.<sup>14</sup>

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# Design and Preparation of Micropatterns for Controlling Stem Cell Functions

Principal Investigator

(Field Coordinator) MANA Scientist MANA Research Associate **Guoping CHEN** 

Naoki Kawazoe Xinlong Wang



#### 1. Outline of Research

Stem cells have attracted tremendous attention in tissue engineering field. Controlling the functions of stem cells remains a great challenge for clinical application of stem cells. Use of micropatterns to control cell morphological features and to study their effects on stem cell functions has shown extremely high potential for stem cell research. In this study, various micropatterns were designed to control cell size, shape and aspect ratio to investigate their influence on cell functions. Stem cells stemness, cell differentiation and nanomechanical properties were investigated using the ingeniously designed micropatterns.

#### 2. Research Activities

A method to prepare precisely controlled micropattern structures was developed by using photo-reactive poly(vinyl alcohol) (PVA). The micropatterns were designed to have different size, shape and aspect ratio. The micropatterns were used for culture of human bone marrow-derived mesenchymal stem cells (MSCs) at single cell level to investigate how the size, shape and aspect ratio affect the functions of stem cells. The morphogenic features of stem cells were regulated by the micropatterns. The stem cells in the micropatterns showed different properties of cell quiescence, stemness and nanomechanics.<sup>1)</sup> The cells with small spreading area and low aspect ratio were more quiescent and softer than their large and elongated counterpart, and they showed higher potential to maintain the multipotency of stem cells. The cells with different shapes showed similar expression level of the stem cell makers. The stemness of stem cells could be controlled by the micropattern structures.

Meanwhile, adhesion and spreading are essential processes of anchorage dependent cells involved in regulation of cell functions. Cells interact with their ECM



Fig. 1. Influence of cell adhesion and spreading in regulating stem cell functions.

resulting in different degree of adhesion and spreading. However, it is not clear whether cell adhesion or cell spreading is more important for cell functions. 10 types of isotropical micropatterns that were composed of 2  $\mu$ m microdots were designed and prepared to precisely control the adhesion area and spreading area of MSCs.<sup>2)</sup> The respective influence of adhesion and spreading areas on stem cell functions was investigated. Adhesion area showed more significant influences on the focal adhesion formation, binding of myosin to actin fibers, cytoskeletal organization, cellular Young's modulus, accumulation of YAP/TAZ in nuclei, osteogenic and adipogenic differentiation of MSCs than did the spreading area. The results indicated that adhesion area rather than spreading area played more important roles in regulating cell functions (Fig. 1).

Furthermore, cellular nanomechanics have been proved to play important roles in regulating cell behaviors with great potential for cancer diagnosis and therapy. Conventional measurement of cell nanomechanics is processed on uniform surfaces. However cells on uniform surfaces lack the control of cellular morphology and size that have significant influence on cell nanomechanics. Control of cell morphology and size is required for precise measurement of cell nanomechanics and elucidation of its relationship with cell structures. The nanomechanics of stem cells, normal cells and cancer cells were compared on the micropatterns.<sup>3)</sup> The three types of cells showed different responses and nanomechanics on the micropatterns. Especially, cancer cells showed less dependence on their microenvironments compared to the stem cells and normal cells. The results suggest that the nanomechanical differences between normal and cancer cells can be used as a biomarker to enhance the diagnosis of cancers. The micropatterned cells showed different behaviors indicating that the cell morphology regulated by micropatterns played critical roles in cell fate determination. All these results proved that the micropatterning technology is useful for manipulation of cell behaviors. And the insights of this study should inspire the design of nanobiomaterials for manipulation of diverse cell functions.

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# Nanotherapeutics Based on Redox Polymer

#### **Principal Investigator**

(Satellite at Univ. Tsukuba, Japan) Lecturer Post-doc Yukio NAGASAKI

Yutaka Ikeda Long Binh Vong, Ahram Kim



#### 1. Outline of Research

The objective of our research is to create new biomaterials for high performance therapy and biodevices. In order to acheve our objectives, we are focusing on elimination of reactive oxygen species (ROS) by our materials. Nitric oxide (NO)-releasing materials are also designed. Using these polymers as a surface coating, nanoparticles and injectable gels, we have confirmed high level of their utilities.

#### 2. Research Activities

#### (1) Radioprotection by redox nanoparticles.<sup>1)</sup>

Radioprotective agents have been developed to protect patients against the damaging and lethal effects of ionizing radiation. However, in addition to the intrinsic ability to target reactive oxygen species (ROS), the ability to retain a significant level of bioavailability is desirable in radioprotective agents because that would increase and prolong their radioprotective efficacy and improve its safety. Here, we developed a novel nanoparticle-based radioprotective agent with improved bioavailability, which suppressed the adverse effects typically associated with low-molecular-weight (LMW) antioxidants. A potent radioprotector could be used for numerous applications including clinical radiotherapy, space travel, radiation site clean-up, radiological terrorists and military attacks, nuclear accidents, and the everyday protection of radiation workers. (2) High performance tissue antiadhesives.<sup>2)</sup>

Postsurgical tissue adhesion formation caused by inflammation and oxidative stress is one of the serious issues because it induces severe clinical disorders. We designed redox injectable gel (RIG), which covalently possesses nitroxide radicals as a reactive oxygen species (ROS) scavenger for high performance tissue anti-adhesion agent. The redox flower micelles exhibiting gelation under physiological conditions were prepared by a polyion complex (PIC) between polyamine-PEG-polyamine triblock copolymer possessing nitroxide radicals as a side chain of polyamine segments and poly(acrylic acid). RIG showed prolonged local retention in the abdominal cavity of the

mice, which was monitored by *in vivo* imaging system (IVIS). Compared with a commercial anti-adhesion agent (Seprafilm<sup>®</sup>, Genzyme, Cambridge, MA), RIG dramatically inhibited the formation of tissue adhesions via a combination of physical separation and biological elimination of generated ROS in talc-induced adhesion model mice.

(3) NO-releasing injectable gels for myocardial infarction treatment.<sup>3)</sup>

Myocardial infarction (MI) is characterized by necrosis of myocardial tissue due to ischemia, and overproduction of reactive oxygen species (ROS) in ischemic myocardium. Nitric oxide (NO), small gas molecule, has been reported to play a critical role in cardiovascular disease. Although NO therapy improves blood flow and neovascularization after MI, due to very short half-life and non-specific distribution, it would be a big limitation for delivery of NO and lowmolecular-weight NO donors as therapy. In addition, ROS in ischemic myocardium facilely interact with NO to form peroxynitrite, and suppress the NO effects. We have recently developed a controllable NO releasing polymer using macrophage-targeted poly(arginine) (PArg) for immunocancer therapy. We previously also developed ROS scavenging redox polymer, which effectively worked on oxidative stress-related diseases. In this study, we developed NO/redox injectable hydrogel (NO-RIG) based on formation of polyion complex (PIC) between cationic polymers [ROS scavenging polymer (PMNT-PEG-PMNT) with macrophage-triggered NO releasing polymer (PArg-PEG-PArg)] and anionic polymer [poly(acrylic acid) PAAc] for cardiovascular disease model mice (Fig. 1).

# (4) Design of antioxidative biointerface for separation of hematopoietic stem cell.<sup>4)</sup>

During cell cultivation, excessively generated ROS affect cellular properties and functions. Although cell cultivation media contain several types of low-molecular-weight antioxidants, these small antioxidants are internalized into the mitochondria and they disrupt regulated redox balance. Here, we developed a novel biointerface that effectively eliminates ROS on a cell culture surface and confirmed effective separation of hematopoietic stem cell with high viability.

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Fig. 1. Injectable hydrogel (NO-RIG) and its application for myocardial infarction mice.

### Nanoarchitectonics-Driven Interfaces and Nanoparticles for Therapeutic Applications MANA Principal Investigator Françoise M. WINNIK

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N. Shirahata

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#### 1. Outline of Research

Our research aims to use Materials Nanoarchitectonics to address current challenges in nanomedicine, placing emphasis on therapeutic agents and diagnostic tools.

#### 2. Research Activities

(1) Formation and spreading of cell-particle hybrid aggregates.

In collaboration with Prof. F. Brochard-Wyart (Curie Institute, Paris, France) and within MANA's "Experiment/ Theory" Challenge, we undertook in 2013 a project aimed at understanding how dead matter (nano and microparticles) affects the behavior of active matter (cell aggregates). We reported the formation of hybrid aggregates; a demonstration that particles can act as nanostickers for cell.<sup>1)</sup> A study of the mechanical properties of hybrid aggregates strengthened our conclusions.<sup>2)</sup>

We study now the spreading of cellular aggregates on "particle carpets" by monitoring their dynamics over 24 hr. When the carpet consists of silica particles 1µm in diameter, the leading cells leaving the aggregates internalize the particles they encounter and "clean" the substrate. A growing aureole of dark particle-loaded cells surrounds the aggregate (Fig. 1A). In contrast, on a carpet of large particles, (SiO<sub>2</sub>, d = 10 um), the lead cells merely push the particles without internalizing them. The aggregates find themselves surrounded by a wall of particles and stop spreading (Fig. 1B). Mechanisms underlying our observations are investigated.



Fig. 1. Spreading of a cell aggregate over a carpet of silica particles  $(A) d=1 \mu m$ : internalization and  $(B) d=10 \mu m$  (microparticles).

#### (2) Smart PNIPAm/cyclodextrin suprastructures.

Photo/thermo-sensitive star poly(n-ispropylacrylamides) (PNIPAm) bearing azobenzene end groups were synthesized and used to prepare supramolecular 3D-networks via inclusion/complexation with a bis( $\alpha$ -cyclodextrin) ( $\alpha$ -CD) linker. Homogeneous aqueous viscous fluids form at 23°C. At 25 °C, they separate into a gel, which occupies < 10 % of the initial volume. The transformation is reversible: upon cooling to 23 °C, the gel expands and recovers its original volume. Under UV light irradiation ( $\lambda$  = 365nm) at 0°C, a 2.5wt% clear star-PNIPAm/cyclodextrin aqueous fluid becomes turbid as a result of the expulsion of cis-azobenzene (the photoproduct) from the  $\alpha$ -CD cavity. Upon irradiation with visible light, the solution recovers its limpidity.

Currently, we are testing structural and environmental factors that affect the swelling/shrinking properties of the suprastructures and we assess possible applications.



Fig. 2. Schematic representation of the preparation of silicon-based luminescent nanomaterials.

#### (3) Silicon-based luminescent nanomaterials.

Silicon- nanomaterials play an increasingly important role in nanomedicine, due to their size- and surfacedependent optical properties, low toxicity, and the high natural abundance of silicon. Given the potential toxicity of waterborne Cd-based quantum dots, silicon nanocrystals (SiNCs) are viewed as safe alternatives. We reported a new synthesis of NIR emitting SiNCs of narrow and tunable photoluminescence (PL) emissions over 700-1000 nm window, endowed of high quantum yields (QYs, >30%) and long PL lifetimes (>300µs) when dispersed in aqueous media.<sup>3)</sup> They consist of a pluronic F127 shell and a core made up of assembled SiNC-OD (octadecyl) (Fg 2, green section). Next we sought to tune their PL spectra via metal doping of the SiNC lattice, which significantly affects their growth and electronic properties, hence alter their PL. Inclusion of < 0.2 % Mn, Ni, Co or Cu atoms shifts the PL of red-emitting SiNCs in the NIR range, opening new opportunities in biomedical imaging responsive to light within the "biological window" as well as to other fields addressable by transition metals (Fig 2, pink section). A third approach is the preparation of amine functionalized water-dispersible silica nanoparticles (NPs) 1-2 nm in diameter.<sup>4)</sup> The NPs are non-toxic and emit intense blue PL without photobleaching. An elevated rate of radiative recombination due to localized surface states present in amorphous silica is believed to be responsible for their high PL intensity with QY > 34% (Fig. 2, red section).

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# Theory behind Nano-Originated Phenomena

Principal Investigator (Field Coordinator) MANA Scientist **Taizo SASAKI** 

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#### 1. Outline of Research

Our ultimate aim is to understand exotic properties and predict nano-structured materials with novel properties by utilizing theories and computational techniques based on the knowledge on nano-originated phenomena. Most of properties of material are in electronic states and/or collaboration among  $10^{23}$  electrons. Thus, we study these issues by applying the quantum mechanics and the statistic mechanics with the aid of the symmetry consideration of the wavefunction and the numerical computations, such as the density-functional theory (DFT) and simulations.

#### 2. Research Activities

#### (1) Symmetry of the electronic states.

As a real material of the topological insulator, we have proposed a member of the two-dimensional compound family MXenes ( $M_{n+1}X_n$ , M: a transition element, X: C or N),  $W_2CO_2$ , on the basis of the DFT calculations. A further search was performed and several new topological insulators were proposed in the MXene family. An extensive quantum fieldtheoretical study<sup>1-4</sup>) was conducted to show how *magnetic counterparts of topological insulators* can be designed using antiferromagnets. These states, which are extremely resilient against perturbations, are nonmagnetic in the bulk while being magnetically active at the surface. We, further, proposed a new kind of symmetry, which is comibinatorial of space and time symmetries, and was not identified in lowenergy regime. This new kind of symmetry would protect energy degeneracies in electronic band structure.

#### (2) Properties of the strongly correlated system.

The magnetic properties of  $CrO_2$ , a popular half-metallic ferromagnet, were studied by combining DFT with the dynamical mean-field theory. Is it argued that its Curie temperature can be substantially increased by the hole doping. This finding can be used in the thin films on the substrate, preventing the material from destroying the ferromagnetism by crystal distortions.<sup>5)</sup> The effects of the doping to the Mott insulator was also studied with the perturbation theory for infinitesimal doping. The results suggest that the doping-induced states in the small-doping limit can essentially be interpreted as the magnetically excited states which appear in the single-particle spectrum because of its charge character.

#### (3) Phase transitions and Cooperative phenomena.

By using a realistic model of Nd<sub>2</sub>Fe<sub>14</sub>B, we successfully reproduced the thermodynamic properties of magnets including the reorientation transition at a low temperature. We also predicted microscopic structures of the magnetic domain wall; At higher temperatures the domain-wall width becomes larger and the magnetization magnitude, smaller, in agreement with experiments. We improved the novel scheme for numerical phase transition study which can be applied to bond-diluted systems. An exponent of the transition in the basic model was evaluated up to the vicinity of the percolation threshold with its bond-density dependence.



Fig. 1. Calculated equation of states of the amorphours phase of BN.

#### (4) Nano-structure of materials.

The nano-structure itself and the interaction with the environments have been important issues. Recently, we have succeeded in the following topics with the first-principles computations:

- It was predicted that the nanostructured TiN(001)/ MgO(001) superlattice exhibit various electronic properties depending on a shape of the TiN dot and a size of the MgO substrate.<sup>6</sup>
- A theoretical method for the water-swelling of ceramics has been developed. It can predict equilibrium swelling-phases of such substances as clay minerals and swollen nanosheets.<sup>7</sup>
- A first-order polyamorphic phase transition between *amorphous* phases of BN have been discovered for the first time,<sup>8)</sup> predicting a discontinuous volume decrease of about 3% under high pressure at 300 K (Fig. 1).
- One of the newly fabricated true-two-dimensional materials, phosphorene, under high pressure was studied theoretically. It proposed an issue how to treat the pressure to the two-dimensional material.

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### Development of O(N) DFT, and Study of Core-Shell Nanowires Principal Investigator David BOWLER

Principal InvestigatorDavid BOV(Satellite at University College London, UK)



#### 1. Outline of Research

Our ultimate aim is to understand advanced nanostructured materials for applications in photovoltaic devices, as well as future electronic devices. Our research combines close collaboration with experiment and theoretical modeling to give a detailed insight into the properties of the materials. In our first satellite project, we investigated how to combine biological inspiration with electronics to give high efficiency materials and solar cells with applications to energy and sustainability. In our present project, we are studying the growth and properties of silicon-germanium nanostructures, both nanowires and clusters formed on surfaces, to optimize their characteristics, particularly concentrating on the mobility and location of dopants. We are also continuing to study biological systems, to seek inspiration for hybrid solidstate/biological nano-architectures.

We are leading the development of *ab initio* methods that can be applied to large systems. Much of our research involves development of the CONQUEST linear scaling DFT code, which has been developed through a long-term collaboration between UCL and NIMS, and is now expanding to include other sites around the world. We have a long-established network of collaboration between MANA in NIMS, and the London Centre for Nanotechnology in University College London. In this year, we have arranged collaborative research visits to MANA for the PI and the MANA UCL student, as well as visits to UCL from researchers in NIMS. We are also expanding our international links, collaborating with the Institute for Molecular Science in University of Bordeaux and Osaka University, in a fourway exchange of personnel and expertise.

#### 2. Research Activities

#### (1) Properties of Semiconductor Nanowires.

We are continuing our work on the growth and properties of silicon nanowires and germanium-silicon core-shell nanowires, in collaboration with Dr. N. Fukata in MANA, who grows the nanowires. Having studied the strain effects in small, hexagonal nanowires, we are now turning to the location and properties of dopants, concentrating on the effects of surfaces and interfaces in the nanowires.

#### (2) Extending ab initio modelling of biomolecules.

We are continuing our work on applying the CONQUEST code to biomolecules. We have recently shown that it is possible to perform high-efficiency molecular dynamics simulations at the first principles level on large systems, and are now starting to test this on biologically-relevant problems. Fig. 1 shows an example, a DNA fragment in water, while Fig. 2 shows the energy for a molecular dynamics simulation performed at constant temperature on this fragment.<sup>1)</sup>



Fig. 1. Structure of a DNA fragment (10 base pairs) in water containing ~3,400 atoms, modelled with CONQUEST.

#### (3) Development of novel methods.

As well as the important area of applications and collaboration with experiment, our research is based around extending and improving the CONQUEST code. We have recently implemented the calculation of stress with linear scaling (a world first), and are actively developing novel approaches to the linear scaling itself.<sup>2)</sup> We also seek accurate, exact methods, and have extended an existing method to allow high quality basis sets with low cost.<sup>3)</sup> The need for methods beyond standard DFT is also important, we maintain our efforts on TDDFT in this area.<sup>4)</sup>



Fig. 2. Kinetic, potential and total energy for the DNA/water system shown in Fig. 1, during a first principles MD simulation.<sup>1)</sup>

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### Development of Large-Scale First-Principles Methods for Theoretical Analyses of Nanoscale Materials Principal Investigator Tsuyoshi MIYAZAKI



#### 1. Outline of Research

We have been developing a large-scale first-principles calculation program called CONQUEST to calculate the structures and physical properties of nanoscale devices or nanostructured materials. Although the first-principles methods based on density functional theory (DFT) are powerful tools to clarify the atomic and electronic structures of materials, conventional DFT methods cannot treat the large systems comprising many thousands of atoms since the calculation cost increases proportional to the cube of the number of atoms N in the system. However, with the CONQUEST code by utilizing a new theoretical technique called linear-scaling or O(N) method, we can perform structural optimization or molecular dynamics simulations of very large systems containing more than a million atoms. With this ability of the code, we can perform theoretical research of actual nanoscale devices or materials at the atomic scale.

#### 2. Research Activities

#### (1) Development of large-scale first-principles methods.

It is important to keep developing new methods and improving the code to explore more applications using CONQUEST. Recently, we have developed a new method to perform efficient and stable molecular dynamics of very large systems with the O(N) DFT method. This method was applied to silicon systems, including the Si/Ge nanowires, and biological systems.<sup>1)</sup> We have also succeeded in developing accurate and efficient basis functions.<sup>2)</sup> This method reduces the cost of the calculations greatly without losing the accuracy. It can be also applied to conventional DFT methods. Since the analysis of electronic structure was difficult in the O(N) DFT method, we also implemented a mathematical method called Sakurai-Sugiura method. With this method, we can now calculate the STM images of the complex surface structures (Fig. 1).



Fig. 1. (a) Optimized structure of a P2 molecule on Si(001). (b) Calculated STM images using Sakurai-Sugiura method (left: occupied, right: unoccupied).

#### (2) Large-scale DFT study on nano-scale materials.

Using the large-scale DFT methods with the CONUQEST code, we now investigate the structural and electronic properties of Si/Ge or Ge/Si core-shell nanowires, in

collaboration with the experimental group headed by Dr. Fukata at MANA. We have calculated the strain distribution in the nanowires and analyzed the electronic structures near the Fermi level using Sakurai-Sugiura method. Fig. 2a shows one of the occupied Kohn-Sham orbitals near the Fermi level. We have found that it is localized in the Ge region. We also study the catalysts of metallic nanoparticles. We have clarified the site dependence of the atomic and electronic structure of gold nanoparticles with various sizes. We work on its reaction properties, especially when they are in the  $O_2$  atmosphere (Fig. 2b).



Fig. 2. (a) One of the occupied states near the Fermi level of Ge/Si core shell nanowire. It is localized in the Ge-core part. (b) Adsorption of SiH4 on O2/Au nanoparticle.

(3) Other Activities: DFT derived force fields by machine leaning etc.

Although we can perform all-atom DFT simulations on very large systems using CONQUEST, we still need a large amount of computation time when we need to search for the structure of complex systems. For this purpose, it is desirable to have cheaper methods which can reproduce the DFT results with reasonable accuracy. Using a machine learning technique, we have constructed a force field learning from the data of atomic forces obtained from the MD simulations by CONQUEST.<sup>3)</sup> We also perform theoretical research of organic solids<sup>4)</sup> in order to clarify the new phenomena from first-principles study.

Development of CONQUEST is done in collaboration with the group of Prof. David R. Bowler (MANA/London Centre for Nanotechnology, University College London).

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# Next-Generation Semiconductor Nanodevices

Group Leader (Nano-Power Field) Naoki FUKATA



#### 1. Outline of Research

Functionalization of semiconducting nanowires by impurity doping is one of the important processes for their application as next-generation field effect transistors and so on. In order to control the dopant concentration, distribution, and electrical activation, it is necessary to characterize the bonding states, electronic states, and electrical activities of dopant atoms.<sup>1-3)</sup> However, the problem of retardation of carrier mobility caused by impurity scattering must be solved if impurity atoms are doped into the channel region.

Core-shell nanowires (NWs) using silicon (Si) and germanium (Ge) appear to have major potential for suppression of impurity scattering. Selective doping and band-offset in Ge/Si and Ge/Si core-shell NW structures can realize a type of high electron mobility transistor (HEMT) structure in one-dimensional NWs by separating the carrier transport region from the impurity-doped region.



Fig. 1. EDX images of (a) i-Ge/p-Si and (b) p-Si/i-Ge core-shell NWs. The red represents Si and blue represents Ge in the EDX images.

#### 2. Research Activities

(1) Structual control of Ge/Si and Si/Ge core-shell NWs.

i-Ge/p-Si and p-Si/i-Ge core-shell NWs were grown by two step growth using chemical vapor deposition. Here, i-Ge/p-Si means intrinsic-Ge/p-type Si. It means that Si shell regions were doped with boron (B). Structural characterization of core-shell NWs was performed by TEM, scanning transmission electron microscopy (STEM), and energy-dispersive X-ray (EDX) measurements. Representative EDX images are shown in Fig. 1. The red represents Si and blue represents Ge in the EDX images. The results clearly show the formation of Ge/Si and Si/Ge coreshell NWs. TEM measurements revealed clear lattice fringes in the core and shell regions.



Fig. 2. Side- and (b) top-view atom maps of a i-Ge/p-Si core-shell NW.

### (2) Distribution of *B* atoms in core-shell *NWs*.<sup>4</sup>

To evaluate the site-selective doping in Ge/Si and Si/Ge coreshell NWs, atom probe tomography was applied first. The atom probe tomography was performed as a collaborative research with Tohoku University. Fig. 2 shows 10 nm-thick atom maps of the side and top views of a i-Ge/ p-Si core shell NW. The atom maps also show the formation of core-shell NW structure.



Fig. 3. Ge optical phonon peaks observed for i-Ge/p-Si. The inset is Band diagram around a Si-Ge heterojunction in Ge/Si coreshell NWs.

(3) Realization of high mobility channel using core-shell NW.

Core-shell NW structures using i-Ge/p-Si and p-Si/i-Ge can separate the carrier transport region from impurity doped region. The demonstration is done by the observation of hole gas accumulation in i-Ge region. To demonstrate the hole accumulation into the i-Ge region in i-Ge/p-Si and p-Si/i-Ge core-shell NWs, we applied Raman spectroscopy. Fig. 3 shows the representative Raman spectra of Ge optical phonon peaks observed for p-Si/i-Ge core-shell NWs. The Ge optical phonon peak also clearly shows the downshift and asymmetric broadening with increased the  $\mathrm{B}_{2}\mathrm{H}_{6}$  gas flux and the shell growth time. This downshift and asymmetric broadening can be explained by the Fano effect.<sup>5)</sup> The Fano effect is due to coupling between discrete optical phonons and the continuum of interband hole excitations in i-Ge region. Hence, the Fano interference shows the hole gas accumulation in i-Ge region in the p-Si/i-Ge core-shell NWs. The same result was also obtained in i-Ge/p-Si coreshell NWs. These results show a conclusive evidence of the hole gas accumulation in Ge/Si and Si/Ge core-shell NWs and realization of one type of high electron mobility transistor structure in one dimensional NWs.

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#### **Biomedical Application of Mesoporous Phospholipid** Particles **Group Leader** Kohsaku KAWAKAMI

(Nano-Life Field)



#### 1. Outline of Research

Safety requirements are very severe for pharmaceutical materials. One of the safest materials as pharmaceutical excipients is phospholipid, which is now used as a constituent of the representative drug carrier, liposome. However, liposome exhibited excellent performance only as an injectable carrier, and it does not function greatly for solid dosage forms. Here we report phospholipidic solid mesoporous particle, which may be used as a novel platform technology for drug delivery. We have established a simple production technology of mesoporous phospholipid particle (MPP) utilizing liquid-liquid demixing to create spherical agglomeration of phospholipid followed by freeze-drying to form mesoporous structure by removing ice crystals. MPP can accommodate both hydrophilic and hydrophobic drugs, and may be used for various administration routes including oral, injectable, nasal, and pulmonary delivery. In this report, preparation method of MPP<sup>1)</sup> and its efficacy as an oral formulation carrier for poorly soluble drugs<sup>2</sup> are introduced.



Fig. 1. Phase diagram of cyclohexane/t-BuOH mixture and a schematic representation of the preparation process of mesoporous phospholipid particles. Solid cyclohexane and t-BuOH are expressed as C(s) and B(s), respectively. Demixing temperature of 6.0% HSPC solution is indicated.

#### 2. Research Activities

Hydrogenated soybean phosphatidylcholine (HSPC) was dissolved in a mixture of cyclohexane and t-butyl alcohol (BuOH) at 50 °C, followed by incubation of the solutions below the liquid-liquid demixing temperature to induce precipitation, which was obtained in a spherical

morphology because of microphase separation. The precipitates were subsequently freeze-dried leading to formation of a mesoporous structure in the particles. Fig. 1 shows the phase diagram of the cyclohexane/ t-BuOH system, on which liquid-liquid phase separation temperature for 6% HSPC solution was plotted.<sup>1)</sup> The onset freezing temperatures of pure cyclohexane and t-BuOH according to thermal analysis were approximately 5.3 and 7.5 °C, respectively, and that of mixtures was lowered by incorporation of the other component. A eutectic point was at t-BuOH/cyclohexane = 1/1 with a freezing temperature of -39 °C. Typically, t-BuOH/cyclohexane = 1/2 solution was used and the precipitation was created at 5 °C. If it was created at 25 °C, particulate precipitates were not obtained because it was above the phase separation temperature.



Fig. 2. SEM (Scanning electron microscopy) image of MPPs. (a) HSPC MPP prepared from cyclohexane/t-BuOH solution, (b) HSPC MPP prepared from cyclohexane/t-BuOH water solution, (c) HSPC/FEN = 9/1 MPP.

Fig. 2 shows SEM images of MPPs.<sup>1,2)</sup> Fig. 2a shows the typical HSPC MPP. The initial HSPC solution can accommodate water to form water-in-oil microemulsions. If MPP was prepared using the microemulsion solutions, particles with totally different morphology was obtained (Fig. 2b). Also presented is the MPP which was prepared with fenofibrate (FEN), a poorly soluble drug. Although porous structure was lost, the spherical structure was maintained (Fig. 2c). In the dissolution tests, FEN was not released in buffered media; however, prompt release was observed when a small amount of surfactant existed. It was because of formation of mixed micelles composed of surfactant and HSPC. In the animal studies, this HSPC/FEN MPP improved oral absorption of FEN compared to crystalline FEN.<sup>2)</sup> The formation of mixed micelles with bile salt seemed to play an important role for enhancing the oral absorption of FEN. Efficacy of MPP in other administration routes is also under investigation.

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# Nanophotonics Devices for Energy Conversion

Group Leader (Nano-Power Field) Tadaaki NAGAO



#### 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. Nanophotonics materials, especially plasmonic materials and metamaterials are now accepted as useful paradigms for materials science which enable us to control flexibly the light in nanospace. In our laboratory, we are designing and developing energy harvesting/onversion devices and materials, especially for highly-efficient photothermal and photocatalyst applications, based on plasmonic and metamaterial concepts. With appropriate electronic structure/dielectric response of the materials themselves, their optimized surface nanostructures, highly efficient photothermal conversion, hot carrier generation as well as high surface electromagnetic field enhancement will be realized.

#### 2. Research Activities

Combination of wide-bandgap oxides or transition metal nitrides with plasmonic nanostructures can provide us broad applications in photoelectric as well as in photothermal energy transduction. For example, by loading metal nanostructures on insulators can generate plasmonicallyinduced hot carriers by visible (VIS) light illumination, and in this way an ultraviolet (UV) active oxide photocatalyst can be converted into a visible (VIS) active photocatalyst (Fig. 1).<sup>1)</sup> Further adopting the concept of metal plamonics to low-loss conductive oxides and conductive nitrides also provides us widened opportunity for handling the light ranging from the infrared region to the visible wavelength region. We are developing some examples of the oxide/ metal nanohybrids for the efficient photoelectric transfer and photocatalysis that combine UV active ZnO and TiO<sub>2</sub> and Mie plasmons of noble metals to generate VIS and near infrared (NIR) catalytic activity.<sup>2)</sup> Also we demonstrate some examples of the photothermal energy transduction by using refractory conductive ceramics or oxide-metal hybrids and their variants for demonstrating the wavelength selective





Photonic/plasmonic Light Absor

Charge separation

Fig. 1. A photonic/plasmonic lattice of metal/oxide nanotube array for efficient solar-light harvesting and charge separation aiming, for example, at water splitting. light emission and absorption in the infrared (IR) region.<sup>3-4)</sup>

Wavelength-selective infrared perfect absorbers, which can absorb 100% of infrared radiation, have great potential for use in various applications such as sensing of organic molecules in liquids and gases, generation of electricity using thermal radiation as an energy source (thermo photovoltaics). Here we have adopted the perfect absorbers for thermal emitters and infrared detectors with wavelength selectivity and high conversion efficiency.<sup>3,5)</sup> We have been metal-insulator-metal type metamaterial developing plasmonic perfect absorbers operating in the midinfrared region. We have realized narrowband IR light emitters using Al as scalable industry-compatible base metal and also Mo and TiN<sup>5,6)</sup> as refractory metals for high-temperature radiative heaters with low-energy consumption. We are also developing wavelength-selective infrared detectors (Fig. 2), or mid-infrared color sensors, for multiband infrared light detection for the applications in various fields, such as for temperature sensing in houses and in offices, night vision applications for auto mobiles, sensors for robot cars, as well as for the applications in homeland security.



Fig. 2. A schematic of the hole-array perfect absorbers combined with pyroelectric ZnO interlayer working as wavelength-selective IR detector. Such IR detectors can be used as infrared multicolor sensor for the temperature sensors and various types of materials sensors.

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# **Development of Photoresponsive Biointerfaces**

Group Leader (Nano-Life Field) **Jun NAKANISHI** 



#### 1. Outline of Research

Biointerfaceis 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).<sup>1-6</sup>



Fig. 1. Photoresponsive biointerfaces developing in this study.

#### 2. Research Activities

(1) Photoactivatable gel substrates for study of mechanobiology of collective cell migration.<sup>3)</sup>

Collective cell migration is migration of cells in a group. It plays critical roles in diverse physiological and pathological processes. In contrast to single cell migration, cluster geometry and sizes are critical factors because they change traction stress distribution within themselves, eventually causing heterogeneous mechanical conditions of each cell. Therefore, to better understand how environmental cues in extracellular matrices (ECM) dictate collective cell migration, it is important to develop a robust platform where biochemical and/or mechanical factors can be controlled in given cell cluster geometries.

In this research, we developed a robust platform for studying the mechanobiology of collective cell migration. Polyacrylamide (PAAm) gel was used as a soft substrate, whose surface was functionalized with photocleavable poly(ethylene glycol) (PEG) (Fig. 2a). Young's modulus of the substrate was tuned close to in vivo soft tissues, while the photoactivatable feature allowed us to analyze migration behaviors of geometrically controlled cell clusters by spatiotemporally controlled irradiation of the surface (Fig. 2b). Such precise geometrical control of cell clusters is critical especially important for collective migration studies because traction stress distribution—major driving force of collective migration—variates depending on cluster geometry as well as the stiffness of the substrate.

As a proof-of-concept, two differently-stiff gel substrates plus glass control were prepared and collective migration behaviors of epithelial cells thereon were analyzed. Our results demonstrated quantitative and qualitative different collective behaviors depending on material stiffness and migration configuration (Fig. 2c). On the other hand, migration behaviors were almost identical when the cells were seeded sparsely as isolated single cells. These facts strongly suggests the observed difference in collective migration behaviors is owing to the emerged mechanical sensitivity when the cells become a group. We believe this physiologically relevant migration assay platform will be useful not only for basic studies of mechanoarchtectonics in collective cell migration, but also for discovering new drugs that regulate cell migration and block tumor expansion.



Fig. 2. Photoactivatable gel substrates: (a) concept, (b) protocol to study migration, (c) representative results.

#### (2) Facile Preparation of Photoactivatable Surfaces with Tuned Substrate Adhesiveness.<sup>4</sup>

In this study, we developed photoactivatable selfassembled monolayers (SAMs) with tuned cell-ECM biochemical interactions because our earlier studies demonstrated significance of adhesive crosstalk in collective cell migration.<sup>5)</sup> The SAMs are composed three disulfides containing either cell-adhesive cRGD, photocleavable poly(ethylene glycol) (PCP), and bioinert hexaethylene glycol (EG<sub>6</sub>). The substrate adhesiveness was controlled by changing the mixing ratio of these components, with minimizing protein adsorption by the EG<sub>6</sub> ligand. The controllability of surface ligand density was validated by cell adhesion and migration tests, complemented with fluorescence observation of an alternative ligand. Depending on the surface ligand density, HeLa cells either kept or lost collective characteristics. The present materials will be useful to address mechanobiology of collective cell migration.

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# Exotic and Functional Molecular Materials

Group Leader (Nano-Materials Field) MANA Scientist Takashi NAKANISHI

Kentaro Tashiro, Shinsuke Ishihara



#### 1. Outline of Research

Frontier Molecules Group has been established in April, 2016, at MANA-NIMS. We focus on synthesis of frontier molecules possessing advanced functions and unique phenomena towards applications in security, sensing as well as bio- medical usage. Our research contains methodologies of molecular design, synthesis, self-assembly, molecular recognition and hybridization with nanomaterials. We are aiming at development of world-top-level functional molecular materials with our original molecular design.<sup>1-3)</sup>

#### 2. Research Activities

#### (1) Blue-colour luminescent novel liquid pyrenes.

The very recent development of solvent-free, nonvolatile, room temperature functional molecule liquids (FMLs) has created an increasing debate on a clear boundary between liquid crystalline fluids and isotropic liquids. The challenge to address the issue falls in determination of the local molecular organization in FMLs. Alternation of number and substitution pattern of bulky and flexible branched alkyl chains on a bluecolour luminescent pyrene unit allows us to study deeper insight of  $\pi$ - $\pi$  interactions in their neat liquid state. Through investigation on photophysical properties of the alkylatedpyrene liquids illustrated homogeneity (monomer emission) or inhomogeneity (intermediate or excimer emissions) in those liquids depending on the extent of pyrene-unit isolation with attached alkyl chains. Our new findings have revealed a novel fluid matter that lies exactly between relatively disordered liquid crystalline fluids and totally disordered isotropic liquids. In addition, stable oil in water microemulsions have been prepared with brightly luminescent liquid pyrene as the sole oil phase.<sup>1)</sup> Small-angle scattering has confirmed the nanoscale structure of the approximately cylindrical microemulsion droplets, which behave as discrete hard sphere at intermediate oil loading. The microemulsions exhibited excimer-rich luminescence, with an emission chromaticity that can be tuned by droplet size.



Fig. 1. A video scene explaining how to synthesize WSMOCAs.

#### (2) How to make WSMOCAs.<sup>2)</sup>

We demonstrate a method for the synthesis of a watersoluble multimetallic peptidic array containing a predetermined sequence of metal centers such as Ru(II), Pt(II), and Rh(III). The compound, named as a water-soluble metal-organic complex array (WSMOCA), is obtained through i) the conventional solution-chemistry-based preparation of the corresponding metal complex monomers having a 9-fluorenylmethyloxycarbonyl (Fmoc)-protected amino acid moiety and ii) their sequential coupling together with other water-soluble organic building units on the surface-functionalized polymeric resin by following the procedures originally developed for the solid-phase synthesis of polypeptides, with proper modifications (Fig. 1). Traces of reactions determined by mass spectrometric analysis at the representative coupling steps in stage (ii) confirm the selective construction of a predetermined sequence of metal centers along with the peptide backbone. The WSMOCA cleaved from the resin at the end of stage (ii) has a certain level of solubility in aqueous media dependent on the pH value and/or salt content, which is useful for the purification of the compound.



Fig. 2. SWCNT-MSP composite sensor for detection of toxic gas.

(3) Wearable toxic gas sensor based on supramolecular nanomaterial and near-filed-communication technology.<sup>3)</sup>

We presented that single walled carbon nanotube (SWCNT) wrapped with metallo-supramolecular polymer (MSP) demonstrates amplified and time-integrated increase in electrical conductivity when disassembly of MSP is triggered by electrophilic chemical substances including diethyl chlorophosphate (DECP), a nerve agent simulant (Fig. 2). The SWCNT-MSP composite material demonstrates over 3000% increase of electronic conductivity upon cumulative exposure to sub-ppm order of DECP, while pristine SWCNT demonstrates negligible response. Owing to an enormous and irreversible sensing response, our material is compatible with a wireless sensing system based on near field communication technology. Thus, commercial smartphone can be employed for facile detection of harmful vapors.

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# Integration of Nano Functionality for Novel Nanosystems

# **Group Leader**

**Tomonobu NAKAYAMA** 

(Nano-System Field, also Administrative Director of MANA) MANA Scientist MANA Research Associate Visiting Scientist Senior Visiting Scientist Graduate Student

Yoshitaka Shingaya, Shigeki Kawai, Hideo Arakawa Rintaro Higuchi, Shrestharekha Goswami Osamu Kubo, Sho Tonegawa Masami Suganuma Li Qiao, Abdul Karim



#### 1. Outline of Research

We develop novel techniques and methodologies toward the realization of novel nanosystems for future information technology. Development and application of advanced scanning probe microscopes such as multiple-probe scanning probe microscopes (MP-SPMs) and fundamental researches on molecular manipulations, low-dimensional nanostructures and neuromorphic networks, are explored. These research contribute to establishing science and technology required for functionalizing nanosystems to transmit, transduce, and even transform electrical, optical, mechanical, ionic and magnetic signals. We are specially interested in spatio-temporal variation of material properties, especially those in nanosystems, because this aspect is an inevitable feature of nanosystems.

#### 2. Research Activities

#### (1) Multiple-probe Scanning Probe Microscopes.<sup>1-5)</sup>

MP-SPM has simultaneously and independently controlled 2 to 4 scanning probes<sup>1)</sup> which are brought into electrical contact to a single nanostructure and reveals its electrical property.<sup>1,2)</sup> Implementation of Kelvin-probe force microscopy (KPFM) mode in our MP-SPM realized noncontact observation of potential distribution over a nanosystem under a current bias. As an alternative noncontact MP-SPM operation, eddy-current damping microscopy (ECDM) mode was successfully introduced by detecting eddy-current induced damping of an oscillating magnetic probe, which is useful to obtain a conductance distribution over the nanosystem. The latest MP-SPM (Fig. 1) equips four angled-long-tip tuning fork probe (Alt-TFP) sensors<sup>3)</sup> and is operated through the home-built control system. This enables combination of different control modes for each probes.<sup>4)</sup> Further improvements regarding spatial resolution of such AFM-based MP-SPM to achieve atomic precision<sup>5)</sup> in locating each probe is required.



Fig. 1. A new MP-SPM with four Alt-TFP sensors, all controlled from an integrated control system. AFM, KPFM, and other force microscopy modes can be combined in this MP-SPM.



Fig. 2. Chemically prepared Ag nanowires (AgNW) covered with insulating PVP layer were used to form neuromorphic networks.

#### (2) Fabrication and characterization of functional nanostructures and nanoarchitectonic systems.<sup>6-7)</sup>

Creating functional nanostructures and nanomaterials, followed by measurements of their physical properties, is an important part of our research towards a realization of functional nanoarchitectonic systems. In this respect, we are currently working on single-molecule-level ultrahigh density data storage using thin films of fullerene C60 molecules<sup>6</sup> and on neuromorphic networks towards braintype computing,. Such networks are prepared by assembling functionalized nanowires into the form of entangled complex network.<sup>7)</sup>

In the case Ag nanowires (AgNWs), we implemented metal-insulator-metal junctions at each crossing point between two AgNWs. Then, we found interesting switching properties as shown in Fig. 2. It is interesting to point out that the observed switching behavior seem to be cooperative property of massive number of junctions involved in the AgNW network. Further investigation on the AgNW network showed the ON and OFF states respectively exhibit different fluctuation nature in the noise of transmitting electrical current. Also, reproducible long-term and shortterm memorization of ON state can be realized by the network, indicating a possibility of a new devices utilizing dynamic noise control.

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### Controlled Modulation of Atomic-Layer Superconductors with Self-Assembled Organic Molecules Group Leader Takashi UCHIHASHI (Nano-System Field)

#### 1. Outline of Research

Recent advancement in nanotechnology has led to realization of two-dimensional (2D) superconductors with truly atomic-scale thicknesses.<sup>1)</sup> Since this is against the general belief that 2D superconductivity cannot exist or should be at least very fragile, the finding is surprising and has attracted much attention. Particularly, we successfully demonstrated the existence of ideal 2D superconductivity, by growing epitaxial indium atomic layers on a silicon surface and by directly measuring macroscopic superconducting currents for the first time.<sup>2)</sup> This surface atomic-layer superconductor was found to have a very high critical current density, and in addition, includes natural Josephson junctions at atomic steps.<sup>3)</sup> These features are preferable in terms of its potential use as a component of superconducting electronic devices.

For practical applications, precise control of the superconducting properties is highly desirable. For this purpose, we have proposed that the self-assembly of organic molecules on 2D superconductors may be employed based on the concept of Material Nanoarchitectonics. As widely recognized, usage of organic molecules is advantageous in terms of flexible and rational designing, which allows a fine tuning of the local interactions at the interface. Furthermore, organic molecules should allow us to add to the system new functionalities such as optical detection. Fig. 1a shows a schematic illustration of the concept. Here the metal atomic layer on a semiconductor surface plays the role of a host 2D material. The adsorbed organic molecules can be the source of charges and spins. This allows them to enhance or suppress the superconductivity of the host material through carrier doping or magnetic effects without structural disruption. We have successfully demonstrated this concept as described below.<sup>4)</sup>



Fig. 1. (a) Concept of a 2D hybrid superconductor consisting of the metal atomic layer (blue spheres) on a semiconductor (grey spheres) and self-assembled organic molecules (on top). (b) Temperature dependences of the 2D resistivity of the indium atomic layer on silicon surface with CuPc overlayer for different molecular coverages ( $0 \le \theta \le 2$  ML). CuPc enhances Tc for  $\theta < 1$  ML.

#### 2. Research Activities

For a 2D superconductor, we used indium atomic layers on silicon, which is technically called the Si(111)-( $\sqrt{7} \times \sqrt{3}$ )-In surface. For the organic molecules, phthalocyanines with Cu and Mn atoms coordinated at center were used (MPc, M = Mn, Cu). In the gas phase, MnPc and CuPc possess spin states S = 3/2 and S = 1/2 respectively. They were found to form nearly identical well-ordered molecular monolayer, which were commensurate with the underlying indium atomic layer.

Unexpectedly, our electron transport measurements revealed that the monolayers of MnPc and CuPc had opposite effects on the superconducting transition temperature (Tc); the Tc shift was negative for MnPc but positive for CuPc (Fig. 1b). Namely, superconductivity is suppressed by MnPc while it is enhanced by CuPc. This distinctive behavior was attributed to a competition of charge and spin effects, based on the results of X-ray magnetic circular dichroism (XMCD) measurements and ab initio calculations. Particularly, the directionality of the d-orbitals of Mn and Cu atoms was found to play a decisive role. The *d*-orbitals of Mn are strongly coupled with the conduction electrons in the indium layer, which leads to strong suppression of superconductivity by magnetic effects. In contrast, the *d*-orbitals of Cu have almost no coupling to the indium layer and does not suppress superconductivity via magnetic effects. This helps to retain the enhancement of superconductivity by carrier doping in the case of CuPc.

The present result indicates that the subtle balance of electronic states within the molecule is crucial in terms of the influence on superconductivity. It also suggests a possibility of locally tuning superconducting properties through manipulation of molecular states. This will open a route for new functionalities based on molecules and superconductors. Currently we are trying to observe the molecular spin effects on superconductivity under high magnetic fields. Non-trivial phenomena such as field-induced superconductivity may occur under such conditions. The coexistence and competition of molecular magnetism, superconductivity, and the Rashba effect on the surface may also lead to rich physics such as topological superconductivity and Majorana fermions.

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### Multi-Functional Electron Tunneling Devices with Molecular Quantum Dots **Group** Leader

(Nano-System Field)

Yutaka WAKAYAMA



#### 1. Outline of Research

Tunneling transistors, which employ the tunneling phenomenon of electrons, attracted attention as possible low power consumption devices from an early date. However, this technology still has not reached practical application because it is necessary to fabricate quantum dots precisely, which are the key constituent element in tunneling transistors, at a size of 10 nm or less. Even today, in spite of progress in micro-fabrication techniques, this is still a difficult challenge. Our research is an attempt to solve this problem by using molecules as quantum dots. Because the size and structure of molecules can be controlled freely, precise design of electronic states is also possible.

Our purpose is to develop electron tunneling devices based on a variety of molecular functions. Functional molecules were integrated into a Si-based architecture, aiming to bridge a gap between fundamental quantum effects and practical device engineering. Here, we demonstrate fundamental mechanism, multi-level tunneling and optical control of electron tunneling. These results were achieved by taking advantages of organic molecules as quantum dots.

#### 2. Research Activities

For practical development, quantum dots for the electron tunneling devices should be well designed on nanometer scale. For example, the size of the quantum dots should be a few nanometers for realizing room temperature operation. Size uniformity is another important factor for fine control of threshold voltage (V<sub>th</sub>). To meet these requirements, we adopted organic molecules as quantum dots. Fullerene (C<sub>60</sub>) molecules were embedded in a MOS structure (Fig. 1(a)). Staircases in current-voltage curves were observed in a double-tunneling junction consisting of Au/Al<sub>2</sub>O<sub>3</sub>/C<sub>60</sub>/SiO<sub>2</sub> multi-layers on Si(100) substrates. Here, C60 and Al2O3, SiO2 layers served as intermediate electrodes and tunneling barriers, respectively. We elucidated that the observed

staircases can be attributed to resonant tunneling through the empty and occupied energy-levels of the C<sub>60</sub> molecules. A schematic energy diagram is illustrated in Fig. 1(b). These results clearly indicate that the  $V_{\text{th}}$  for electron tunneling can be tuned precisely as requested by designing molecular structure.1

We applied this mechanism to various functional tunneling manipulation those are multi-level tunneling<sup>2</sup> and optical switching<sup>3)</sup> of electron tunneling. First, phthalocyanine molecules with different molecular structures, the energylevels of which were precisely tuned by attaching electrondonating (or withdrawing) substituents, were embedded in the MOS structure. Multi-level tunneling according to the energy-levels of respective phthalocyanine was successfully observed, demonstrating potential of multi-value memory or switching devices. Second, a reversible photochromic reaction (open-ring/closed-ring isomerization) of diarylethene was applied for optical switching. Here, the energy-levels of respective isomers can be reversibly changed by alternate UV and visible light irradiation in accordance with reversible conformational change in photochromic molecules. In our device, switching of electron tunneling was achieved upon these light irradiation, demonstrating an optical memory effect in the electron tunneling device.

Importantly, our device configuration is compatible with that of a conventional MOS-FET device and, therefore, these results demonstrate the potential of practical use of molecules for the energy-saving tunneling devices in the Sibased devices, such as single-electron memory, multi-level tunneling switching device and photon-electron converter.

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Fig. 1. (a) Device and molecular structures. (b) Energy-level diagram, showing resonant tunneling.

### Relative/Absolute Nanomechanical Sensing towards **Mobile Olfaction Group** Leader

(Nano-Life Field)

Genki YOSHIKAWA



#### 1. Outline of Research

Demands for new sensors to detect or identify target molecules are rapidly growing in various fields, such as food, agriculture, medicine, security, and environment. Nanomechanical sensors have potential to contribute to these global demands owing to their intrinsic versatility. Based on the recently developed platform "Membrane-type Surface stress Sensor (MSS)",10 we are now trying to realize useful nanomechanical sensor systems which can fulfill the practical requirements, such as portability, low-cost, ease of use, in addition to the basic specifications, e.g. high sensitivity and selectivity. We have also developed new analysis method "Aero-Thermo-Dynamic Mass Analysis (AMA)",<sup>2</sup> which provides another approach to characterizing gases by measuring molecular weight in ambient condition without a vacuum or ionization. The combination of MSS and AMA will provide both relative and absolute information on target gases, achieving comprehensive characterization.

#### 2. Research Activities

#### (1) Smell identification of spices using MSS.<sup>3)</sup>

To realize an artificial olfactory system, not only an array of chemical sensors but also a valid feature extraction method is required. In the present study, we demostrated the identification of spices by smell using MSS. Both static and dynamic features were extracted from the sensing signals obtained from four MSS coated with different types of polymers, focusing on the chemical interactions between polymers and odor molecules. The principal component analysis (PCA) of the dataset demonstrated the separation of each spice on the scatter plot, which reflects the chemical composition of the vapors (Fig. 1). It is also important to note that we demonstrated the identification of samples by pure smell which is not affected by undesired components such as solvent vapors.



Fig. 1. PCA scatter plot of MSS signals of various spices.



Fig. 2. Relationship between molecular weights of various gases and deflection of the micro-cantilever based on the AMA concept. The results of experiments (red circles), FEA, (blue circles), analytical model (dotted gray line) converged on a single line.

#### (2) Aero-Thermo-Dynamic Mass Analysis.<sup>2)</sup>

Each gas molecule has its own molecular weight, while such a microscopic characteristic is generally inaccessible, and thus, it is measured indirectly through e.g. ionization in conventional mass analysis. We have developed a novel approach to the direct measurement of molecular weight through a nanoarchitectonic combination of aerodynamics, thermodynamics, and mechanics, transducing microscopic events into macroscopic phenomena. It is confirmed that this approach can provide molecular weight of virtually any gas or vaporizable liquid sample in real-time without ionization. Demonstrations through analytical calculations, numerical simulations, and experiments verify the validity and versatility of the novel mass analysis realized by a simple setup with a flexible object (e.g. with a bare cantilever and even with a business card) placed in a laminar jet (Fig. 2). Owing to its unique and simple working principle, this aero-thermo-dynamic mass analysis (AMA) can be integrated into various analytical devices, production lines, and consumer mobile platforms, opening new chapters in aerodynamics, thermodynamics, mechanics, and mass analysis.

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### Smart Nanofibers for Cancer Therapy

Associate Principal Investigator Mitsuhiro EBARA (Nano-Life Field)



#### 1. Outline of Research

We developed a smart anticancer nanofiber that is capable of simultaneously performing thermotherapy and chemotherapy for treating malignant tumors. By tailoring the nanoarchitectures of polymer networks in the fiber, we demonstrated simultaneous heat generation and drug release in response to an alternating magnetic field (AMF).<sup>1,2)</sup> A 5–10-min application of AMF alone successfully induced cancer apoptosis in both *in vitro* and *in vivo* studies.



Fig. 1. Schematic illustration for the nanofiber-based treatment of basal cell carcinoma.

#### 2. Research Activities

Squamous cell carcinoma is an epithelial malignant tumor found in mucous membranes lined by stratified squamous epithelium and in the skin. At present, the main therapeutic methods are surgery, radiation therapy, and chemotherapy, according to the cancer stage. In recent years, thermotherapy (or hyperthermia), which takes advantage of the fact that cancer cells are more sensitive to heat than normal cells, has attracted widespread attention. Since thermotherapy is also effective for enhancing drug efficacy and relieving pain, there are high expectations of its combined use with chemotherapy and other treatments. In this research, we developed a mesh material that can be applied directly to the affected site and is capable of simultaneously performing thermotherapy and chemotherapy for treating epithelial malignant tumors (Fig. 1). The nanofiber is composed of a



Fig. 2. SEM and TEM images for the electrospun nanofiber mesh. Magnetic nanoparticles were successfully incorporated within the fiber.

chemically crosslinkable, temperature-responsive polymer combined with an anticancer drug and magnetic nanoparticles (MNPs), which serve as a trigger of drug release and a source ofheat, respectively (Fig. 2). By tailoring the nanoarchitectures of polymer networks in the fiber, the nanofiber mesh shows switchable changes in the swelling ratio in response to alternating "on-off" switches of the AMF because the selfgenerated heat from the incorporated MNPs induces the deswelling of polymer networks in the nanofiber. Correspondingly, the on-off release of drug from the nanofibers is observed in response to the AMF. Both in vitro and in vivo studies showed that the majority of tumor cells died after only a 5–10-min AMF application due to the double effects of heat and drug (Fig. 3).



Fig. 3. Excised tumors from different treatment groups at day 56. First, lung cancer cells (NCI-H23) were injected to SCID mice. After cell inoculation, the tumor was allowed to grow to a volume of 50–150 mm<sup>3</sup>. Then, nanofiber mesh was implanted subcutaneously near the tumors. AMF was applied to the mice every 7 days for a total of 8 times. After 2 months, the weight and size of the tumors in all mice were recorded.

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# Synthesis and Assembly of LDH Nanosheets

Associate Principal Investigator Renzhi MA

(Nano-Materials Field) Internship student

Wei Ma, Pengzhan Sun, Yishun Zhong, Yifan Lin, Hao Wan, Fashen Chen



#### 1. Outline of Research

Various layered compounds undergo exfoliation or delamination under suitable conditions, yielding molecularly thin nanosheets. The ultimate two-dimensional (2D) anisotropic feature of nanosheets can radically increase the accessible surface area, and induce peculiar chemical and physical properties. Similar to a LEGO game, we have been working on the design and fabrication of nanocomposites based on different kinds of functional nanosheets. This strategy can be regarded as a typical example of nanoarchitectonics.

For example, as shown in Fig. 1, positively charged layered double hydroxide (LDH) nanosheets can be alternately stacked or sandwiched with oppositely charged building blocks, e.g., graphene oxide (GO), to form superlattice-like composites. Our previous study has demonstrated that the nanocomposites may be used as active electrode materials to develop hybrid supercapacitors capable of storing or releasing huge energy in very short time, i.e., seconds. They have also been assessed as promising nonprecious electrocatalysts for efficient water splitting: electrochemical decomposition of water (H<sub>2</sub>O) into oxygen (O<sub>2</sub>) and hydrogen (H<sub>2</sub>).



Fig. 1. LDH nanosheets can be hetero-assembled with graphene (oxide) into superlattice-like nanocomposites utilizing an electrostatic charge-driven approach.

#### 2. Research Activities

(1) Synthesis of transition metal bearing LDH nanosheets.<sup>10</sup>

LDH materials, with a most representative composition of magnesium-aluminum  $(Mg^{2+}-Al^{3+})$  hydroxide, are traditionally regarded as a clay phase, which is benign to the environment and human body. They have been used for applications such as adsorbents, polymer additives or drug delivery systems. To endow this traditional clay mineral with more versatile functions, we have developed a range of synthetic methods to produce brand new LDHs incorporating various mixed transition metal cations, such as Mn, Fe, Co, Ni, and Zn. Through subsequent soft-chemical exfoliation, single-layer nanosheets with controllable composition, e.g., Ni<sup>2+</sup>-Fe<sup>3+</sup> and Ni<sup>2+</sup>-Mn<sup>3+</sup>, have been newly prepared (Fig. 2). They are emerged as a novel class of attractive 2D materials to explore exciting electronic, magnetic, electrochemical and catalytic properties.



Fig. 2. Atomic force microscopy (AFM) images of single-layer nanosheets bearing different transition metal compositions. Photographs show Tyndall effect of the nanosheet suspensions.

# (2) Highly selective charge-guided ion transport through a LDH/GO hybrid membrane.<sup>2)</sup>

We have fabricated a hybrid membrane consisting of cationic Co-Al (or Mg-Al) LDH nanosheets and anionic GO superlattice units. The experiments on concentration gradient-driven ion diffusion through the membrane showed that the cations bearing various valences can be effectively separated according to their charges strictly, independent of the cationic and charge-balancing anionic species. The relative selectivity of the hybrid membranes towards monovalent (Z=1) and trivalent (Z=3) cations was as high as 30 times (Fig. 3). Such a high selectivity could not be achieved by GO multilayer stacks, LDH nanosheet multilayer ones or their bulk stratified membranes, indicating that the molecular-level hetero-assembly of GO and LDH nanosheets indeed induced a synergistic effect and played a unique role in the high-performance ion separation processes.



Fig. 3. Comparison of diffusion coefficients (normalized by AlCl<sub>3</sub>) for different valent cations (Z=1-3) through a hybrid GO/Co-Al LDH nanosheet membrane.

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# Materials for Functional Nanomedicine

Managing Researcher (Nano-Life Field)

#### Hisatoshi KOBAYASHI



#### 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 mimic this system to create highly functional biomaterials for several application.

#### 2. Research Activities

(1) Ultrastructure analysis of pre- and post-implanted samples of decellularized corneas prepared by highhydrostatic pressurization.

We have reported that the fabrication of the decellularized cornea for corneal stroma regeneration using high hydrostatic pressure (HHP) method.<sup>1,2)</sup> Compared with detergent decellularization methods, features of cornea such as mechanical properties and glycosaminoglycan (GAG) content were well maintained in HHP decellularization method. The xenogeneic implantation experiment showed very good results such as good enough mechanical properties, high transparency, very low immunological reaction after 1 year after implantation. In those studies, we found that after HHP treatment, decellularized cornea became opaque. It did not affect the high-performance of the HHP-decellularized cornea, however, it is necessary for the reason of that for further application. For the reasons, it was speculated that after HHP treatment, only water content change in HHP treated cornea induced the opaque change and ultra-structure of the collagen were preserved after treatment. A cornea is a rare transparent and mechanically strong tissue in the living body. The transparency and strength of cornea is based on the high order architecture of collagen fiber which are main constituents to optical lattice. Such sophisticated structure was very sensitive to outsides environment. In this study, to investigate our hypothesis, the ultra-structures of pre- and -post implanted HHP treated-corneas were analyzed by scanning and transmission electron microscope.

Porcine corneas were taken, immediately after resection, corneas were washed using antibiotics containing PBS and preserved using above antibiotics containing PBS adding 3.5 % w / v dextran at 4 °C until used. Fabrication of HHP decellularized cornea as follows; corneas were put into high pressure machine (Kobe Steel, Ltd., Kobe, Japan) and applied 10,000 atm for 10 minutes at 10 °C. Then, pressurized corneas were washed using EGM-2 medium containing 0.2



Fig. 1. Structure analysis of decellularized cornea.<sup>39</sup>

mg / ml DNase I, same antibiotics with and 3.5 % w / v dextran at  $37 \degree$ C for 72 hours under 5% CO<sub>2</sub> atmosphere with shaking. HHP decellularized cornea also tested using two kind of animal transplantation model. Decellularized cornea was transplanted into corneal stroma of Japanese white rabbit (female, 2.5-3.0 Kg, 12 weeks old). Animals were handled according to the ARVO statement on the use of animals in ophthalmic and vision research. All animals were approved by the ethical committees for animal welfare of National Institute for Materials Science (Tsukuba, Japan) and Tokyo Medical and Dental University (Tokyo, Japan).

The corneal substrates became transparent just within week after the implantation and showed good biocompatibility. And it also has good mechanical properties, as it can be suturing by surgical suture. These properties are quite different from current collagen-based corneal substitute; it was much more superior to that of current one. Here we demonstrated the ultrastructure of decelluralized corneal stroma by high-hydrostatic pressurization was relatively preserved before and after implantation (Fig. 1).<sup>3)</sup>

We concluded that the superior properties of the decellularized cornea, which prepared by high-hydrostatic pressurization, such as better mechanical strength and optical characteristics, were originated from the preservation of the superstructure of the treated cornea.

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# Characterization and Control of Defects

Managing Researcher (Nano-Materials Field)

#### Takashi SEKIGUCHI



#### 1. Outline of Research

We have been 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. We are characterizing 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 electrooptics 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.

#### 2. Research Activities

#### (1) Switching mechanism of $SrTiO_3$ (MD EBIC).

SrTiO<sub>3</sub> has been attracting much interest for the application of resistance random access memory (ReRAM). Resistance switching is observed in metal/SrTiO<sub>3</sub> junctions. The mechanism of this switching is, however, not clarified yet. We have observed Nb-doped (111) SrTiO<sub>3</sub> using EBIC technique.<sup>1)</sup> Dislocations exhibited dark EBIC contrast at room temperature suggesting the presence of recombination centers. When changing the bias condition or accelerating voltage, bright EBIC contrast was observed around certain dislocations (Fig. 1). It is considered that dislocations in SrTiO<sub>3</sub> are associated with different defect levels depending on their characters. Dislocations with line vector of [111] tend to have shallow levels and maybe relate to the resistance switching.



Fig. 1. EBIC images of dislocations in (111) SrTiO<sub>3</sub> at (a) 0 V and (b) -2 V. Bright contrast appeared around dislocations.

#### (2) Cross sectional CL of SiAlON phosphers (Anything CL).

Rare-earth doped SiAlON phosphors have great potential for phosphor application. Wavelength tunable luminescence can be obtained by changing the rare-earth ions and their concentration in the host lattice. However, due to the difficulties of sintering conditions, SiAlON phosphors often



Fig. 2. Cross-sectional-CL images at 300 nm (red), 430 nm (blue) and 540 nm (green) (a) and local CL spectra taken at 5 kV for a Ca doped JEM phosphor.

contain secondary phases. We performed cross-sectional CL observation using cross sectional polishing (CP) method.<sup>2)</sup> The luminescence and element distribution in the particles were identified by low-voltage CL microscopy and electron prove micro analyzer (EPMA). Fig. 2 presents the CP-CL measurement of Ca-doped JEM ((La,Ce)Al(Si<sub>6-z</sub>Al<sub>z</sub>)(N<sub>10-</sub>  $_zO_z)(z\sim1)$ ) blue-phosphors. Submicron grain emits 540 nm luminescence along a large portion of the particles with dark grain boundary, while another portion emits 430 nm luminescence. The 300 nm emission is locally distributed. Based on the literature and XRD analysis, we can attribute the band centered at around 430 nm to Ce<sup>3+</sup> in JEM and that at 480 nm to  $Ce^{3+}$  in  $\alpha$ -SiAlON. The darker broad emission is originated to  $Ce^{3+}$  in  $\beta$ -SiAlON, and that at 310 nm to SiAlON host material. This result indicated that JEM phosphor consists of many different phases agglomerated with each other. The secondary phases induced the red shift and the broadening of spectrum.

Recently, the 3-dimensional output of CL data has been developed (Fig. 3). The superiority of this technique will be demonstrated in the coming year.



Fig. 3. 3D representation of CL data.

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# Nano-Device Materials and Lithium Ion Batteries

Senior Scientist with Special Mission (Nano-Theory Field)

#### Takahisa OHNO



#### 1. Outline of Research

Our aim is to understand the formation mechanism and the structure-property relationship of nano-materials for applications in advanced electronic devices and batteries, as well as to develop the simulation methods including the first-principles (PHASE/0 code<sup>1)</sup>), classical, and multi-scale methods which can be applied to large systems. We are now studying the growth mechanism of graphene nanostructures, the growth and properties of oxide layers on silicon carbide (SiC), the interface properties of lithium ion battery materials, the structures and properties of membrane electrode assembly (MEA) of polymer electrolyte fuel cell (PEFC) and so on.



Fig. 1. Snapshots from the constrained MD calculations for a carbon atom incorporation to the ZZ edge on the Cu(111) slab.

#### 2. Research Activities

#### (1) CVD Graphene Growth on Cu Surfaces.

Graphene has attracted considerable research interest owing to its potential application to future electronic devices such as high speed transistors, transparent electrodes, chemical sensors, etc. These device applications urge establishing synthetic routes to obtain graphene films of large area and high quality. Amon several methods used to produce graphene, the chemical vapor deposition (CVD) method using transition metal catalysts is the most suitable for commercial graphene production, as it can create large area graphene films with low cost. We have studied the



Fig. 2. Calculated potential profile for a carbon atom incorporation to the ZZ edge on the Cu(111) slab. The energetics of reactions was analyzed in terms of potential of mean force by the blue moon (BM) method.

carbon atom reactions in CVD processes for graphene production on Cu surfaces (Fig. 1) by the blue moon (BM) method based on the first principles molecular dynamics (MD) simulations at typical CVD growth temperatures at ~1000°C.<sup>2)</sup> This study focuses on the processes of a carbon atom incorporation to graphene edges. The energy barriers of these carbon atom incorporation reactions have been calculated as ~ 1 eV (Fig. 2), which are comparable or slightly larger than the barriers of carbon atom dimerization. We have also found that the surface copper atoms form step like structures to terminate the carbon dangling bonds at graphene edges, which are markedly different from the graphene-copper interactions observed in static calculations.



Fig. 3. Atomic structure of the interface between the cathode (LiFePO<sub>4</sub>) and sulfide solid electrolyte (Li<sub>3</sub>PS<sub>4</sub>) materials in all-solid-state lithium ion batteries.

#### (2) Interface properties of lithium ion battery materials.

All-solid-state lithium ion batteries (LIBs) are expected to be the next-generation energy storage devices because of their high energy density and good safety performance. However, the all-solid-state LIBs tend to show low power density, which comes mainly from the high ionic resistance at the interfaces between cathodes and sulfide electrolytes. To elucidate the origin of the high interface resistance we have theoretically investigated the properties of the cathode interfaces with the sulfide electrolyte and oxide electrolyte for comparison.<sup>3)</sup> From the density functional molecular dynamics simulations of the LiFePO<sub>4</sub>/Li<sub>3</sub>PS<sub>4</sub> interface (Fig. 3) in both discharged and charged states, we have demonstrated the instability of the sulfide interface in the charged state, that is, the lithium depletion and oxidation on the sulfide side near the interface, in contrast to the oxide interfaces. The obtained results imply the formation of a Lidepleted layer around the sulfide interfaces during charging and support the validity of the insertion of oxide buffer layers at the interface to reduce the interface resistance.

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# Laser-Based Photoemission Spectroscopy

**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 solid surfaces and two-dimensional systems. Currently, we concentrate on developing laser photoemission spectroscopy (PES) into a novel technique to probe surface dynamics.<sup>1)</sup>

Spin orbit interaction (SOI) is a key for controlling the electron spin without nonmagnetic materials. Solid surface and interface, in which inversion symmetry is broken, is an important field to control SOI. For example, it is well known that the lifting of spin degeneracy occurs by a Rashba type SOI at solid surfaces. (The Rashba hamiltonian is described as  $H_R \propto \alpha_R \sigma(\hat{z} \times p)$ .) Since Rashba effects at surfaces have been observed, many researchers have investigated SOIrelated systems as a key factor in realizing spintronics devices. Although many studies have relevant revealed the SOI in occupied states, only few studies report SOI in unoccupied states. However, the SOIs in the unoccupied states are also important, especially for integrating spintronics with photonics. And a methodology to investigate them is required to be established. Thus, one of our purposes of this study is developing angle-resolved two-photon photoemission spectroscopy for investigating the SOI in the photoexcited (unoccupied) states and demonstrating that its powerfulness.



Fig. 1. Schematic energy diagram for CD-2PPE. The helicity of the IR polarization determines the spin direction of the electrons excited preferentially.

#### 2. Research Activities

(1) Rashba Splitting in Image Potential State Investigated using Circular Dichroism Two-Photon Photoemission

#### Spectroscopy.

We have constructed a very high energy-resolved twophoton photoemission system, and then investigated the SOI characteristics (Rashba splitting) in the image potential states (IPSs) of Au(001). To highlight the Rashba effect in IPS, we have combined circular dichroism (CD) measurements with two photon photoemission (2PPE) spectroscopy (CD-2PPE). Schematic diagram of CD-2PPE is shown in Fig. 1a.



Fig. 2. Spectroscopic data for CD-2PPE experiments on Au(001) (a) CD-2PPE spectra of Au(001). The dotted curve denotes the Lorentz function fit that determines the peak position. The inset in each panel shows a magnified view of the rectangular area to highlight the difference in peak positions. (b) The experimental geometry for the spectra shown in (a). (c) All the data for the angle-resolved 2PPE spectra of Au(001). The upper (lower) panel shows the data probed by the RCP (LCP) light. (d) The peak position versus k<sub>i</sub>. The green circles (orange crosses) are the results corresponding to the LCP (RCP) light.

Fig. 2 summarizes the CD-2PPE results<sup>1)</sup> of Au(001). As shown in Fig. 2, we have succeeded in identifying the SOIinduced (Rashba type) band splitting of the image potential state on Au(001). The measured CD characteristics are consistent with those obtained from theoretical calculations based on the density functional theory with the embedded Green's function technique, which describes the electronic states of semi-infinite crystals. We expect that this technique would contribute to the quest for materials that exhibit large spin-polarized photocurrents.

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### Thermodynamic and Thermoelectric Properties of Organic Dirac Fermion System Independent Scientist Takako KONOIKE



#### 1. Outline of Research

Since the discovery of graphene in 2004, it has been attracting a great deal of interest because the electrons in graphene behave like massless Dirac fermions. In contrast with normal electrons with parabolic energy band structure, Dirac fermions show various anomalous behaviors resulting from the peculiar liner dispersion, so-called Dirac cone. However, its experimental study, especially the thermal measurements are particularly difficult because the sample is atomically thin and tiny to detect the reliable signal amplitude. It is now become evident that such a liner dispersion is realized not only in graphene, but also in some organic conductors, and surface states of topological insulators. In particular, organic conductor  $\alpha$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub> is known to be a first bulk crystal which realizes a massless Dirac fermion system under high pressure. By taking advantage of its bulk nature, we experimentally study the thermodynamic and thermoelectric properties of Dirac fermions in this organic compound.

#### 2. Research Activities

Organic conductor  $\alpha$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub> is composed of organic molecule BEDT-TTF and inorganic anions I<sub>3</sub>. These molecules are stacked alternatively and forming a multi-layered structure of conducting and insulating layer, respectively. At ambient pressure, this compound is semi-metallic and undergoes semiconductor-insulator transition at 135 K accompanied by charge ordering. By pressuring the sample above 15 kbar, the charge ordering state is suppressed and then the Dirac cone dispersion appears in the energy band structure. Here, we will show the experimental results of the specific heat and the thermopower of this material at 15 kbar.

#### (1) Specific Heat of Organic Dirac fermion system.

In usual metals, the electronic specific heat is proportional to temperature, as is well known. In contrast, we found that the temperature dependence of the specific heat of  $\alpha$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub> at 15 kbar without background signal from pressure medium shows almost quadratic behavior at low temperature (Fig. 1).<sup>1)</sup> It strongly suggests the linear energy dispersion in this system. This is the first experimental result of the specific heat in massless Dirac Fermions. In a magnetic field, the specific heat first increases with magnetic field, begins to decrease with the peak structure, and then finally saturates in a high magnetic field. These behaviors can be understood by assuming the existence of the zero-mode Landau level characteristic of the Dirac fermion system and its Zeeman splitting. These results are quite consistent with the reported magnetoresistance in this compound.

#### (2) Themopower of Organic Dirac fermion system.

In the thermopower measurements, we also obtained anomalous behavior associated with the massless Dirac



Fig. 1. Temperature dependence of specific heat of  $\alpha$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub> at 15 kbar.

fermions. We observed the giant Nernst effect which is dominant rather than the Seebeck effect in the quantum limit region (Fig. 2).<sup>2)</sup> This unusual behavior results from the intrinsic nature of the zero-mode Landau level, which consists of both electrons and holes. Even more surprisingly, the signal amplitude is quite large compared with that of graphene. The possible origin of the giant signal is the sharp Landau level structure in organic conductor due to the high-purity crystal, and thermal excitation between the adjacent spin-splitted Landau levels of N=0 and 1. Our data can be well reproduced by the theoretical calculations with the reasonable parameters for this compound.<sup>3)</sup> These results show that high-purity organic crystals of  $\alpha$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub> can provide an ideal testing ground for experimental studies of massless Dirac fermions.



Fig. 2. Density plot of Nernst signal of  $\alpha$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub> at 15 kbar..

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### Multi-Responsive Porphyrin/Polymer Systems for Sensing Applications Independent Scientist Jan LABUTA



#### 1. Outline of Research

Porphyrins are widely studied functional dyes that can coordinate a great variety of metal cations. In biological systems, porphyrins play essential roles as photosynthetic antenna and reaction center, in heme proteins as an oxygen carrier, and as vitamin B<sub>12</sub>. In our research we use porphyrin derivatives for various sensing applications such as enantiopurity sensing,<sup>1-3)</sup> selective detection of anions or determination of trace water impurities in organic solvents.<sup>4,5)</sup> Most of these sensing features are realized by non-covalent interactions (H-bond, electrostatic,  $\pi$ - $\pi$ , etc.) between porphyrin and substrate (analyte). The sensing is unfortunately permitted only in organic solvents (CHCl3, THF, DMSO, etc.). Therefore, we have introduced water soluble moieties such as tetraethylene glycol (TEG) or poly(*N*-isopropylacrylamide) (**PNIPAAm**) at the periphery of porphyrin (TPP) functional unit (Fig. 1). These porphyrin/polymer systems exhibit response to whole range of stimuli (temperature, pH, solvent composition, etc.) and are potential candidates for various sensing applications.



Fig. 1. Structures of two examples of water soluble porphyrins.

#### 2. Research Activities

#### (1) Phase behavior.

The results show that upon heating above ca. 50 °C (**TEG-TPP** in  $H_2O$ ) the system undergo reversible phase separation (Fig. 2a). This phenomenon is also known as lower critical solution temperature (LCST) behavior or cloud point transition (CPT). These porphyrins also exhibit reversible protonation depending on pH of solvent (Fig. 2b) which is accompanied with color change from purple-red to green and change in geometry of macrocyclic core from flat to saddle-like shape. Another interesting property is cononsolvency (Fig. 2c). This is manifested as a phase separation dependent on composition of binary solvent (H<sub>2</sub>O/DMSO) mixture at constant temperature (i.e. the porphyrin derivatives are soluble in neat H<sub>2</sub>O or DMSO but insoluble in 50:50 H<sub>2</sub>O:DMSO mixture).

#### (2) Sensing and potential applications.

There are only a few examples reported of phaseseparable small molecules with well-defined structure and functionality.<sup>6</sup> Our porphyrin derivatives combine rich field of porphyrin sensing properties with another large area of phase behavior (LCST) which is usually considered the



Fig. 2. (a) Temperature response (phase separation) in TEG-TPP/ water system. (b) Reversible pH response accompanied with color change and transition of porphyrin core. (c) Solvent composition response (co-nonsolvency).

domain of polymers.<sup>7</sup> Numerous applications of polymers are under current investigation in areas such as controlled drug release and delivery, bio-separation and others. The extension of the LCST phenomenon from polymeric to the non-polymeric supramolecular field will lead to the development of novel 'smart' materials for specific sensing, detection, separation and imaging purposes in aqueous media. For example, in situ monitoring of variation of enantiomeric excess (ee) in enantioenrichment reactions (Soai-type reactions), racemization reactions or conversion of pharmaceuticals during biological processes (Fig. 3). Also the possibility of pH variation or physical filtration based on LCST phenomenon may find interesting applications. In addition, these compounds can be potentially used in photodynamic therapy (PDT) or for heterogeneous catalysis when metal cation is introduced to porphyrin center.



Fig. 3. Schematic visualization of in vivo enantiomeric excess (ee) mapping of chiral metabolites using MRI.

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# Molecular Self-Assembly by Dewetting

**Independent Scientist** 

**Takeo MINARI** 



#### 1. Outline of Research

Control the wetting of a thin liquid film on a solid surface has been crucial in the rapid development of a number of practical situations such as painting, dyeing, metal or glass anticorrosive treatment and lubrication. The wetting phenomena are also critical for printed electronics devices which have attracted considerable interest owing to their high compatibility and ease of integration.<sup>1-3)</sup> We developed the simple and useful methods to manipulate the solution droplets by controlling wetting and dewetting phenomena on solid surface, which enabled us to form 1-dimentional structures or 2-dimentional crystalline films of organic semiconducting materials. These films exhibited high fieldeffect mobility in thin-film transistors.

#### 2. Research Activities

# (1) Vapor driven wetting and dewetting for 1-dimentional microstructures.

Wetting of the droplet into a thin liquid film on a certain solid surface followed by solvent drying is the crucial process for the nanostructure formation. However, such a thin liquid film was commonly observed to rupture due to the instability on a given surface. Here, we developed the vapor driven wetting (VDW) technique to control the dynamical kinetics of a solution droplet by the co-solvent vapor, which yielded a reversible spreading/dewetting process between the spherical droplet and the stable thin liquid layer on a lyophobic surface<sup>4)</sup> (Fig. 1). We found that the anisole droplet first spreads under co-solvent vapor of cyclohexane even on the lyophobic surface, then starts receding due to drying. As the solvent recedes, we can form highly-aligned 1-dimentional structures of functional materials such as nanowires and organic semiconductors at the three-phase contact (TPC) line. Our theoretical model indicates that the wetting process was governed by the



Fig. 1. (a) and (b) Schematic illustration of preparing in-plane aligned nanowire arrays and organic crystals using VDW, respectively;
(b) and (d) Image of in-plane aligned silver nanowires and Cs-BTBT nanofibers observed in polarized optical microscope, respectively. Inset in (b), image taken by scanning electron microscopy.

sorption of co-solvent vapor within the droplet, which alters the surface free energy, lowers the contact angle, reduces the liquid film thickness, and stabilizes the drying process. The obtained thin liquid films allow the in-plane alignment to generate one-dimensional nano- or micro-structures in deposited materials, such as nanowires and organic crystals. In particular, in-plane aligned organic single crystals unveiled a high field-effect mobility achieved up to 9.1 cm<sup>2</sup>/ Vs in thin-film transistors.

# (2) Unidirectional dewetting of micro droplet arrays for high mobility OTFTs.

Unidirectional dewetting enables the production of large-area thin films in high efficiency at low cost. Here we developed the simple method to control the unidirectional dewetting on large-area microdroplet arrays (MDAs), which was induced via the gravity-induced deformation in droplets combined with alternating lyophilic/lyophobic patterns. The MDAs were prepared by surface wettability contrast guided by a printed lyophobic polymer layer including wettable bank regions. It was found that increase of substrate tilted angle enabled the deformation of droplets, thus leading to the homogeneous receding of upper TPC lines from top to bottom on the MDAs. The unidirectional dewetting allowed the deposition of highly-crystalline discrete organic semiconducting thin films in large area, which can be applied for fabrication of fully-printed OTFT arrays (Fig. 2). The resulting fully-printed OTFTs exhibited the fieldeffect mobility of 13.1 cm<sup>2</sup> V<sup>1</sup> cm<sup>-1</sup> for C<sub>8</sub>-BTBT.



Fig. 2. Unidirectional dewetting of organic semiconductor ink by gravity-assisted dewetting. (a) Schematic illustration of aligned organic film formation by gravity-assisted dewetting. (b) Deposited aligned film of TIPS-Pentacene on printed Source/ drain electrodes.

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### GaN Polarization Engineering for Power Electronics Application MANA Independent Scientist Liwen SANG



#### 1. Outline of Research

Compared with the Si and GaAs semiconductors, III-V nitrides have a higher breakdown voltage, larger saturation velocity, higher carrier mobility and higher thermal stability, which enabled them not only suitable for full-spectrum optical devices, but also promising for the high-power and high frequency electronic devices. However, there are sill challenges in the high-quality film growth and effective *p*-type doping, which hinders the development of nitride devices.

The objective of this research is to utilize the unique polarization engineering in III-V nitride field, and fabricate high-power electronic devices. We will introduce our work on the polarization-induced two-dimensional hole gas (2DHG) for *p*-channel InGaN/GaN field effect transistors (FETs) and near ideal vertical-type Schottky barrider diodes (SBDs) on MOCVD-GaN/GaN substrate.<sup>1)</sup>

#### 2. Research Activities

# (1) The first P-channel InGaN/GaN MOSFETs for complementary power ICs.

The conventional Si-based power electronic devices are approaching material limits. On the other hand, widebandgap semiconductor GaN provides a better choice for the power electronics industry as a result of the much higher breakdown field (over 10 times) with lower on-resistance (1/100), higher carrier mobilities, high temperature stability and more compact in size (1/1000). However, compared to the fast development of AlGaN/GaN n-channel high electron mobility transistors (HEMTs), the performance of the p-channel FETs is still far from the integration fabrication. We developed the first *p*-channel metal-oxidesemiconductor field effect transistors (MOSFETs) by using InGaN/GaN heterojunctions. The 2DHG was successfully extracted from the heterojuntion, and the devices can be working at temperature as low as 8K due to the temperature independence of 2DHG (Fig. 1). Compared to the AlGaN/ GaN p-channel FETs, this structure has several advantages: higher holes mobility and concentration, easy integration without crack problem, wide-range working temperatures,

and feasibility of normally-off operation during growth. This work opens a promising route for the development of nitride one-chip complementary integrated circuits.

#### (2) Near ideal vertical-type SBDs fabricated from MOCVD-GaN/GaN substrates.

GaN has attracted much attention for their potential applications in power electronic devices, benefitting from its superior properties, such as wide band gap, high electron mobility, large breakdown field and high thermal conductivity. A vertical structure is believed to be more suitable for high-power applications than lateral devices since high current and voltage can be achieved simultaneously with reduced on-resistance and less effect from surface/interface states. Moreover, the fast development of free-standing GaN substrates with low threading dislocations (TDs) density (on the order of  $10^6$  cm<sup>-2</sup> or less) in recent years opens up an opportunity for the GaN verticaltype power conversion applications. Compared to PN junction diodes, the Schottky Barrier diodes (SBDs) are expected to achieve both low on-resistance and turn-on voltages since they do not have minority carrier storage issue and have higher electron mobility. To obtain highperformance power electronics, carbon incorporation during MOCVD growth is an important issue.

We detailed investigate the effect from growth rates of the GaN drift layer on free-standing GaN substrate by changing the TMG flow rates. It was found that, nearly all the characteristics, including the yellow band intensity, mobility and morphology of the GaN drift layer, the Schottky properties, such as ideality factor, barrier height, specific on-resistance, turn-on voltage, were strongly dependent on the growth rates. An optimized growth rates from 2.62 to 7.78  $\mu$ m/h was observed for a high-quality drift layer with high mobility (>1000 cm<sup>2</sup>/Vs) and SBDs with near ideal Schottky property (n=1.03) with low on-resistance (0.75 m $\Omega$  cm<sup>2</sup>) and turn-on voltage (0.69 V) (Table I).



Fig. 1. P-channel InGaN/GaN MOSFETs.

Growth rate (µm/h)	Ideality factor	Φ (eV) From I-V	Free carrier Density (cm <sup>-3</sup> )	$R_{on}$ (m $\Omega$ ·cm <sup>2</sup> )	Mobility (cm²/V·S)
2.61	1.12	0.935	6.35E+15	0.75	1371
4.45	1.03	0.934	2.30E+15	2.63	1008
7.78	1.04	0.854	3.10E+15	2.90	638
8.08	1.59	0.693	4.59E+16	0.83	279

Table I. Key SBDs parameters extracted from electrical property.

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### Green Nanochemistry: Bandgap Engineering for Group IV Nanostructures Independent Scientist Naoto SHIRAHATA



#### 1. Outline of Research

A prospective research scenario of optics and optoelectronics including development of light emitting diodes, solar cells, and lasers utilizes self-standing nanocrystals of semiconductors to attain improved performance of devices and combined technology with printing techniques for advanced wearable devices. Findings of strong luminescence from nanostructures of group IV semiconductors and their compounds, i.e., Si, Ge, Si<sub>x</sub>Ge<sub>1-x</sub>, 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 those light-emitters 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 green & sustainable future.

#### 2. Research Activities

# (1) Origin of the PL QYs Enhanced by Alkane-Termination of Freestanding Silicon Nanocrystals.<sup>1)</sup>

On the basis of the systematic study on temperature dependence of photoluminescence (PL) properties along with relaxation dynamics we revise a long-accepted mechanism for enhancing absolute PL quantum yields (AQYs) of freestanding silicon nanocrystals (ncSi).

A hydrogen-terminated ncSi (ncSi:H) of 2.1 nm was prepared by thermal disproportination of  $(HSiO_{1.5})_n$ , followed by hydrofluoric etching. Room-temperature PL AQY of the ncSi:H increased twentyfold only by hydrosilylation of 1-octadecene (ncSi-OD). Combinational analysis of the evolution of bandgap energy with PL decay dynamics as a function of temperature suggested that the confinement of photogenerated electron-hole carriers in the ncSi is strengthened by termination with alkyl monolayers to yield the enhanced PL AQY. A combination of PL spectroscopic measurement from cryogenic to room temperature with structural characterization allows us to link the enhanced PL AQYs with the notable difference in surface structure between the ncSi:H and the ncSi-OD. According to the Raman spectroscopic study, the surface layer of the ncSi:H was significantly distorted under structural reconstruction to generate an amorphous phase whereas the passivation with alkyl monolayers suppresses the surface reconstruction to hold a bulky-like geometry, i.e., diamond cubic lattice structure, in a broad range from the center toward nearsurface in the ncSi. HAADF-STEM study confirmed the amorphization that occurs at the surface of the ncSi:H. Such a structurally disordered region possibly works as a nonradiative relaxation channel to give a low PL AQY.

Interestingly, the passivation with alkyl monolayers works to prevent the undesired surface reconstruction, leading to the high PL AQY.



Fig. 1. Double-shelled structure of water-borne ncSi-based NPs. (b) Changes of PL Intensity as function of time for the NPs dispersed in water, PBS solution, and PBS solution with BSA (c) Micrograph of NIH3T3 cells observed with confocal fluorescence microscopy.

#### (2) Functional Double-Shelled Silicon Nanocrystals for Two-Photon Fluorescence Cell Imaging.<sup>2)</sup>

Functional near-IR (NIR) emitting nanoparticles (NPs) adapted for two-photon excitation fluorescence cell imaging were obtained starting from octadecyl-terminated silicon nanocrystals (ncSi-OD) of narrow photoluminescence (PL) spectra, no long emission tails, continuously tunable over the 700-1000 nm window, absolute PL quantum yields of 30-48%, and PL lifetimes of 300  $\mu$ sec or longer. Fig. 1a shows the molecular design of the water-soluble NPs. Moreover, the NPs retained their colloidal stability and emission characteristics for extended periods under physiological conditions (pH 7.4, 0.1M NaCl) in the presence of serum albumin, the major protein in blood (Fig. 1b). The NPs, consisting of a Pluronic F127 shell and a core made up of assembled ncSi-OD kept apart by an OD layer, were readily internalized in the cytosol, but not the nucleus, of NIH3T3 cells (Fig. 1c) and were non-toxic. Asymmetrical flow field flow fractionation (AF4) analysis was carried out to determine the size of the NPs in water. HiLyte Fluor 750, amine was linked via an amide linkage to NPs prepared with Pluronic-F127-COOH, as a first demonstration of functional NIR-emitting water dispersible ncSi-based nanoparticles.

Overall, the ncSi reported here present all the critically important features of currently used compound semiconductor QDs, but without looming toxicity issues. The ncSi nanoparticles are amenable to in-vitro and, potentially, in-vivo imaging within the "biological" optical window.

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# **Computational Design of Photofunctional Materials**

**Independent** Scientist

**Naoto UMEZAWA** 



#### 1. Outline of Research

Solar light is a promising solution to the ever-increasing demand for renewable energy. Solar energy can be converted into electrical and chemical energy by means of photovoltaics and photocatalysis, respectively. In this regard, it is imperative to develop solar energy harvesting materials with good photoabsorption. Such photoabsorbers should possess an electronic structure with a forbidden energy gap, the so-called "band gap", for efficiently harvesting solar light and generating photoexcited electron-hole pairs. Computational methods have emerged as a powerful tool for the design of energy band structures for semiconductor materials with photoabsorbing capacity.

#### 2. Research Activities

#### (1) A metal sulfide photocatalyst composed of ubiquitous elements for solar hydrogen production.<sup>1)</sup>

A visible-light-sensitive tin sulfide photocatalyst was designed based on a ubiquitous element strategy and density functional theory (DFT) calculations. Computational analysis suggested that tin monosulfide (SnS) would be more efficient than SnS<sub>2</sub> as a photocathode for hydrogen production because of the low ionization potential and weak ionic character of SnS (Fig. 1) To test this experimentally, nanoparticles of SnS were loaded onto a mesoporous electrode using a wet chemical method, and the bandgap of the synthesized SnS quantum dots was found to be tunable by adjusting the number of successive ionic layer adsorption and reaction (SILAR) cycles, which controls the magnitude of the quantum confinement effect. Efficient hydrogen production was achieved when the bandgap of SnS was wider than that of the bulk form.



Fig. 1. Band alignment of SnS and SnS<sub>2</sub> estimated from our density functional theory calculations.

(2) Electronic properties of highly-active  $Ag_3AsO_4$ photocatalyst and its band gap modulation: an insight from hybrid-density functional calculation.<sup>2)</sup>

The electronic structures of highly active Ag-based oxide photocatalysts Ag<sub>3</sub>AsO4 and Ag<sub>3</sub>PO<sub>4</sub> are studied by hybriddensity functional calculations (Fig. 2). It is revealed that

Ag<sub>3</sub>AsO<sub>4</sub> and Ag<sub>3</sub>PO<sub>4</sub> are indirect band gap semiconductors. The Hartree-Fock mixing parameters are fitted for experimental band gaps of Ag<sub>3</sub>AsO<sub>4</sub> (1.88 eV) and Ag<sub>3</sub>PO<sub>4</sub> (2.43 eV). The smaller electron effective mass and the lower valence band edge of Ag<sub>3</sub>AsO<sub>4</sub> are likely to be responsible for the superior photocatalytic oxidation reaction to Ag<sub>3</sub>PO<sub>4</sub>. The comparable lattice constant and analogous crystal structure between the two materials allow the opportunities of finetuning the band gap of Ag<sub>3</sub>As<sub>x</sub>P<sub>1-x</sub>O4 using a solid-solution approach. The development of Ag<sub>3</sub>As<sub>x</sub>P<sub>1-x</sub>O4 should be promising for the discovery of novel visible-light sensitized photocatalysts.



Fig. 2. Projected density of states (PDOS) on each atomic specie in (a) Ag<sub>3</sub>PO<sub>4</sub> and (b) Ag<sub>3</sub>AsO<sub>4</sub>. (c) Schematic diagram for As–O and P-O bonding.

(3) Controlling the Electronic Structures of Perovskite Oxynitrides and their Solid Solutions for Photocatalysist.<sup>3)</sup> Band-gap engineering of oxide materials is of great interest for optoelectronics, photovoltaics, and photocatalysis applications. In this study, electronic structures of perovskite oxynitrides, LaTiO<sub>2</sub>N and SrNbO<sub>2</sub>N, and solid solutions,  $(SrTiO_3)_{1-x}(LaTiO_2N)_x$ and  $(SrTiO_3)_{1,x}(SrNbO_2N)_x$ , are investigated using hybrid density functional calculations. Band gaps of LaTiO<sub>2</sub>N and SrNbO<sub>2</sub>N are much smaller than that of SrTiO<sub>3</sub> owing to the formation of a N2p band, which is higher in energy than the O2p band. The valence- and conduction-band offsets of SrTiO<sub>3</sub>/LaTiO<sub>2</sub>N and SrTiO<sub>3</sub>/ SrNbO<sub>2</sub>N are computed, and the adequacy for H<sub>2</sub> evolution is analyzed by comparing the positions of the band edges with respect to the standard hydrogen electrode (SHE). The band gap of (SrTiO<sub>3</sub>)<sub>1-x</sub>(LaTiO<sub>2</sub>N)<sub>x</sub> and (SrTiO<sub>3</sub>)<sub>1-x</sub>(SrNbO<sub>2</sub>N)<sub>x</sub> solid solutions are also discussed.

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### Probing Light-Matter Interaction at the Atomic Scale, inside the Transmission Electron Microscope ICYS-MANA Researcher Ovidiu CRETU



#### 1. Outline of Research

The last few decades have witnessed considerable efforts towards energy production from renewable sources, as well as towards technologies which improve energy efficiency. Among these efforts, an important research direction concerns materials which convert between electricity and light.

The objective of the present research is to aid the development of light-converting and light-producing technologies through the identification of novel nanomaterials by studying their interaction with light, down to the atomic scale. This is accomplished by visualizing the combined effects of light emission and absorption with electrical measurements on individual nano-objects, allowing for their improvement towards the goal of integration in next-generation devices.

Experimentally, the research plan is based on a technique which allows for an optical fiber and a sharp metallic electrode to be positioned with nanometer precision, and interact with individual nano-objects, inside a transmission electron microscope (TEM). This system is used to investigate light-production and light-absorption for low dimensional semiconducting nanowires.

#### 2. Research Activities

# (1) Development of a system which allows simultaneous TEM imaging and CL spectroscopy.

The schematic layout of the system is illustrated in Fig. 1a. A multi-mode optical fiber is connected to a piezoelectric tube, which allows for its positioning close to the region of interest of the sample with sub-nanometer accuracy, using a piezo-controller unit. A voltage source is connected to the scanning coils of the microscope and controls the focused electron beam, which is scanned across the region of interest. The electrons interact with the sample and produce several signals: photons are collected by the optical fiber and transferred to a spectrometer. The scattered electrons are collected by an electron detector. Both these signals are acquired simultaneously and mapped across the region of interest. An image of the end-section of the TEM holder is shown in Fig. 1b.



Fig. 1. a) Schematic layout of the experimental set-up. b) Optical image of the end-section of the holder, highlighting the locations of the main components.



Fig. 2. a) Annular dark-field image of the end-section of a nanowire.b) CL spectrum obtained from this region. b1-b6) Spatial distribution of the amplitudes of the Gaussian components of the spectrum.

#### (2) CL hyperspectral mapping of CdS nanowires.

Fig. 2a shows the simultaneously-acquired dark-field image of a nanowire, while Fig. 2b depicts a cathodoluminescence (CL) spectrum acquired in this section. There is significant variability between signals coming from areas found in close proximity to each other. The spectrum is fitted using a series of Gaussians, whose amplitudes' distributions are shown in Figs. 2b1-b6.

In the absence of doping and in view of the singlecrystal nature of our samples, the primary candidate structures responsible for the various peaks observed are atomic-scale intrinsic defects. By analyzing previouslypublished results, we can assign the 520-530 nm region to S interstitials, 600-650 nm region to Cd interstitials, 680-770 nm region to S vacancies, and finally the 1000-1030 nm region to Cd vacancies. By relating the above with photoluminescence (PL) measurements, we can conclude that the as-grown nanowires contain primarily defects under the form of Cd interstitials. The electron beam creates additional defects corresponding to two regions: between 500 and 550 nm - corresponding to S interstitials - and between 650 and 800 nm - corresponding to S vacancies. Considering the experimental conditions and calculations concerning irradiation damage in this material, we estimate one S vacancy every 50x50 nm<sup>2</sup> and one Cd vacancy every 135x135 nm<sup>2</sup>. These values lead to very low defect concentrations, but which can act as luminescence centers.

Our results reveal the distribution of luminescence centers in this material with nanometer-precision. These centers are associated to various intrinsic defects in CdS, which allows mapping these defects even when their concentration is below the level detectable by other traditional techniques, providing new insights into the nature and distribution of defects in CdS nanowires.

# Doped Diamond Multilayers for High Power Devices

**ICYS-MANA Researcher** 

**Alexandre FIORI** 



#### 1. Outline of Research

The electrical application of doped diamond multilayers is an innovative way to counteract a resistivity too large for building competitive high power devices.<sup>1)</sup> By doing so, we expect to combine large current densities (100 A/cm<sup>2</sup>) and high breakdown voltages (10 MV/cm). Boron doping modifies diamond electrical properties from semiconductor to conductor, and even superconductor at low temperatures. As example, the alternate of heavy and light boron-doped films will modulate electric band structures and dielectric permittivity.<sup>2)</sup>

Another advantage of doped diamond multilayers concerns its crystal lattice structure, which can be manipulated due to large dopants covalent radii. As a result, strain and stress can be engineered within doped diamond multilayers to provide dislocation-free epilayers. For instance, crystalline dislocations are responsible of premature breakdown. If successful, results will be beneficial for unipolar and bipolar high-power devices.



Fig. 1. Schematic of the integration of doped multilayer inside a diamond Schottky diode for high electrical power applications.

#### 2. Research Activities

#### (1) Electrical properties of diamond multilayers.

Diamond multilayers composed of nm-thin films with different doping levels are tested as conductive buffer, which once capped by a drift layer (lightly boron-doped) complete a "push-trough" Schottky diode (Fig. 1). Deep etching process over several micron is required in order to contact electrically such device. We also focused the investigation of etching processes by plasma or catalysts.

#### (2) Heavy boron doping of diamond by CVD.

The accuracy of thickness and boron doping stand on slow deposition rate. To do so, the carbon fraction in the gas feeding the CVD plasma was reduced. However, we face to difficulties under small carbon fractions: boron incorporation efficiency saturates, and etchant features were observed. We realized that chemical reactions supporting diamond CVD were modified by the conjunction of large boron fractions with small carbon fractions in the feed gas. We performed a plasma diagnostic by optical emission spectroscopy (OES), and we found a correlation between diamond etching and the non-linear intensity of BH\* peak (433 nm). OES is use to monitor the continuous CVD of doped diamond multilayer by adjusting atomic fractions in the feed gas (Fig. 2).



Fig. 2. Chronogram of gas flow rates and normalized OES intensity of C<sub>2</sub>\* and BH\* peaks during the continuous CVD of diamond boron-doped multilayer. (Total gas flow rate = 250 sccm).

#### (3) Dislocations in diamond and metallic interfaces.

Collaborations with Institut Neel / CNRS at Grenoble (France), and with the University of Cadiz (Spain) were centered on the study of dislocations and metallic interfaces (Schottky contact). Thick boron-doped diamond multilayers been have elaborated on pre-shaped buffers in order to investigate growth anisotropy, and the genesis of dislocations in various directions.<sup>3)</sup> These results feed the data base to further control strain and dislocations inside doped diamond multilayers.

Concerning metallic interfaces, the oxygen termination of diamond prior to metal deposition appears to be critical for stable operations under high temperatures. The atomic composition of diamond/metals (WC and Zr) interfaces has revealed that interfacial oxygen redistribution, and skin oxide formation had radical effects on ideality factors and the homogeneity of Schottky barrier heights.<sup>4</sup>

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### Interpretation of Nanomechanical Sensing Signals toward Artificial Olfaction ICYS-MANA Researcher Gaku IMAMURA



#### 1. Outline of Research

Olfaction is the only human sense that has not been artificially realized as a practical sensor because of its complex perception mechanism. In analogy with the human olfactory system, an artificial olfactory system should have two main processes: detection and identification. First, odor molecules are detected by an array of chemical sensors. Then, the smell is identified from the sensing signals through a certain protocol. For such an artificial olfactory system, a nanomechanical sensor is an optimal platform owing to its high sensitivity and high versatility. Many studies using nanomechanical sensors have succeeded in smell identification. However, more valid identification protocols based on the detection principle of nanomechanical sensing must be developed to achieve high validity and reliability.

#### 2. Research Activities

(1) Analytical models for nanomechanical sensing signals.

A nanomechanical sensor consists of two parts: a substrate and a receptor layer. When the sensor is exposed to



Fig. 1. (a) Comparison between the theoretical model and an experimentally obtained sensing signal. (b) Gas identification using extracted parameters.

a sample gas, gas molecules are absorbed on a receptor layer and the resultant stress is transduced as a signal. Since the absorption dynamics reflects the chemical interaction between gases and receptor materials, several intrinsic properties can be extracted from the transient behavior of the sensing signal. M.J. Wenzel *et al.* proposed a theoretical model for a polymer-coated cantilever and extracted viscoelastic properties from experimentally-obtained sensing signals. While their theoretical models are given in differential equations, these equations can be analytically solved in some special cases. In this study, we have derived analytical solutions for a cantilever model and extracted intrinsic parameters simply by fitting sensing signals with the analytical solutions (Fig. 1a). We have also demonstrated gas identification from the extracted parameters (Fig. 1b).



Fig. 2. PCA score plot of the dataset.

# (2) Smell identification of spices using nanomechanical membrane-type surface stress sensors.

We demonstrated identification of spices by *smell* using nanomechanical membrane-type surface stress sensors (MSS).<sup>1)</sup> On the basis of the principle of nanomechanical sensors, features were extracted from the sensing signals obtained from four MSS coated with different types of polymers. By focusing on the chemical interactions between polymers and odor molecules, parameters that reflect both static and dynamic phenomena were utilized for analysis. The results of principal component analysis (PCA) on the dataset consisting of the extracted parameters shows that the spices are separated from each other on the scatter plot, depending on the chemical composition of *smell*—volatile organic compounds (VOCs) in the vapor of the spices (Fig. 2).

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### Electron-State Engineering of Atomic-Layer Materials Thin Films ICYS-MANA Researcher Thanh Cuong NGUYEN



#### 1. Outline of Research

Atomic-layer nanomaterials such as graphene, boronnitride or transition-metal dichalcogenide are of great interesting owing their unique physical/chemical properties. For practical application of these materials for electronic devices, it is necessary and important to control the physical and chemical properties of atomic-layer materials under realistic environments such as external electric field, chemical doping, substrate, etc. Based on the computational materials science, we demonstrate the possibility to tuning the electron-states of transition-metal dichalcogenide materials for high thermoelectric performance or superconducting channel for nanoelectronic devices by electrostatic or chemical doping.

#### 2. Research Activities

#### (1) Atomic-layer materials for thermoelectric devices.

Thermoelectric devices can directly convert waste heat into electric power, and they are one of the most important technologies that are considered future sustainable energy sources. Low dimensional materials such as atomic-layer materials such as transition-metal dichalcogenides  $MX_2$  (M=Mo, W, X=S, Se) are expected to exhibit the high thermoelectric performance due to the quantum confinement effect. In collaboration with Prof. T. Takenobu (Nagoya University), large thermoelectric power factor (>200  $\mu$ Wm<sup>-1</sup>K<sup>-2</sup>) in MoS<sub>2</sub> and WSe<sub>2</sub> monolayers that was one order of magnitude larger than that of bulks has been achieved<sup>11</sup> (Fig. 1).



Fig. 1. (a) A schematic depiction of thermopower measurement, (b) Carrier-density-dependent power factor of WSe<sub>2</sub> monolayer, and (c) The theoretical and experimental Seebeck coefficients of WSe<sub>2</sub> and MoS<sub>2</sub> monolayers under electron/hole doping.

By using density functional theory, we developed a theoretical model that permits us to estimate accurately the Seebeck coefficient, then thermopower factor. In combination with experimental data, we clarified the effect of carrier doping concentration on the Seebeck coefficient to find a optimized carrier density for high thermoelectric performance. The large enhancement of thermoelectric power factor is attributable to the step-function-shape density of state at the valence or conduction band edges. By electron/hole doping process, the carrier density dramatically changes that induce the large Seebeck coefficient or thermopower factor. These results suggest the atomic-layer materials such as transition-metal dichalcogenides  $MX_2$  are promising materials for high performance thermoelectric devices.



Fig. 2. (a) Electronic band structure, (b) wavefunction distribution of the  $\alpha$ -state at  $\Gamma$ -point, and (c) Fermi surface of Potassium doped MoS<sub>2</sub> layer.

#### (2) Superconducting atomic-layer materials.

We also demonstrate that electron-state of MoS<sub>2</sub> monolayer also is tunable by chemical adsorption of potassium (K) atoms on the  $MoS_2$  surface.<sup>2)</sup> We find that the unoccupied nearly-free-electron (NFE) state of MoS<sub>2</sub> also shifts downward with increasing the concentration of doped potassium, and crosses the Femi level at the concentration of  $10^{15}$  atom/cm<sup>2</sup> (Fig. 2) due to the strong local electric field induced by charge transfer from K atoms to MoS<sub>2</sub> layer. On the other hand, the NFE state is known to exhibit the floating character with the maximum amplitude distribution in vacuum region where the atoms are absent. Therefore, this NFE-state with its floating characteristics acts as a conducting channel, leading superconducting behavior, as in the case of graphite intercalated compounds. In other word, by chemical doping process, MoS<sub>2</sub> layer could act as a superconducting channel in the electronic devices.

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### Neuromorphic Hardware – Inorganic and Organic Based Neuromorphic Arrays ICYS-MANA Researcher Curtis James O'KELLY



#### 1. Outline of Research

Integrated semiconductor devices have driven the information age for the last half century ushering the modern era of interconnectivity. Data is generated at an exponential rate through various platforms such as social media, search engines and the internet of things (IOT). Many new and exciting insights into our society in this modern age can be obtained from analyzing these data using techniques such as statistical analysis and machine learning.

Machine learning is a powerful analysis technique for identifying patterns and recognizing emerging trends. Adaptability and learning are programed at the software level using traditional semiconductor hardware. Neuromorphic hardware based on memristors however seeks to emulate the adaptability and cognitive ability of the brain to produce learning with adaptability at the device hardware level.

Unlike traditional semiconductors which are static and unchanging neuromorphic hardware displays the ability to change and adapt its properties in response to stimuli such as voltage pulses and light.<sup>1)</sup> This ability to adapt directly mimics the brains neural synapses. Discovering new neuromorphic materials and novel computational paradigms to exploit their properties are the focus of this research.

#### 2. Research Activities

#### (1) Novel Neuromorphic Hardware Materials.

There remains plenty of scope for discovering new types of memristive materials beyond common transition metal-oxides (TMO's) such as TiO<sub>2</sub>, HfO and TaO that may display properties beyond resistance switching. Inorganic nanowires are simple to produce and can demonstrate unique neuromorphic properties.<sup>2)</sup> Initial results on ZnO nanowire arrays shown in Fig. 1 reveal memristive properties such as continuum conductance based on voltage pulse history necessary for building neuromorphic arrays.

#### (2) Organic Memristive Materials.

Work on organic nanowire arrays has yielded exciting new results similar to those observed for ZnO and other inorganic nanowire memristors (Fig. 2). This novel observation has the potential to drive new research in the field of neuromorphic hardware derived from the large catalogue of organic materials published in the literature Inorganic Nanowire Based Memristor



Fig. 1. ZnO nanowire networks dispersed on an interdigitated electrode substrate. Consecutive voltage sweeps at the same bias direction alter the conductance of the network relative to the voltage pulse time and amplitude. Leveraging these properties are ideal for producing neuromorphic arrays.



Fig. 2. Organic nanowires dispersed on an interdigitated electrode display similar properties to inorganic wires when tested under the same conditions.

and their uniquely tailorable synthesis compared to inorganic nanowires.

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# Nanostructured Surfaces and Plastics

**ICYS-MANA Researcher** 

**Gaulthier RYDZEK** 



#### 1. Outline of Research

Fundamental properties of self-assembled nanostructured surfaces obtained by electro-click chemistry have been studied. A second prominent research axis consists on increasing our fundamental understanding of plastics made of polyelectrolytes, with a focus on their ionic exchange abilities.

#### 2. Research Activities

# (1) Nanostructured surfaces assembled by electro-click chemistry.

Hybrid nanocapsules with a 100 nm diameter were synthesized by using iron oxide nanoparticles and either an alkylated or azidated polyacrylic acid polymers. The resulting building blocks allowed assembling films by using an electro-click deposition approach.<sup>1)</sup> A copper(I) catalyzed alkyne-azide coupling reaction was performed by electrochemistry, in presence of the hybrid nanocapsules, and Cu(II) (Fig. 1). This process resulted in the growth of nanostructured films, in one step and one pot, and whose composition and thickness could be tuned (Fig. 1). The potential of these nanostructured hybrid films for vectorization processes and controlled release is under investigations in collaboration with Rennes University.



Fig. 1. Schematic depiction of the electro-click deposition process of a film composed of hybrid nanocapsules (left). SEM micrograph of the resulting film obtained after 30 min deposition (right).

#### (2) Bulk plastics from polyelectrolytes.

Competing with hydrogels, a new research field is emerging with the processing of bulk materials composed of polyelectrolytes complexes plasticized by salts (COPECs). Impact on several fields, including catalysis, energy sparing and biomaterials, is expected. A collaborative project is now beginning to assess how these materials are reacting to changes of their environment. COPEC based on polyallylamine hydrochloride (PAH) and polymethylacrylic acid (PMA) in the presence of NaCl exhibited macromeso- and micro-structural changes upon ionic exchange of NaCl with CuCl<sub>2</sub> at constant ionic strength. This process experimentally resulted in a swelling of the COPEC concomitant to an increase of its hydration level (Fig. 2).

Quite unexpectedly, the ionic exchange process



Fig. 2. Evolution of the chemical composition of PMA/PAH COPECs, in terms of molalities, during the ionic exchange process of NaCl with CuCl<sub>2</sub>.

ultimately lead to an accumulation of more ions in the COPEC than it initially contained (measured *via* the ionic strength on Fig. 3). This could both originate from an internal reorganization of the polyelectrolyte chains, offering more extrinsic charge compensation sites, or from the deactivation of the ions through the formation of oxides/ hydroxides. In any case, the critical point where the ionic strength begins to exceed its initial value coincides with a dramatic decrease of the COPEC's thermal and hydration properties (Fig. 3).



Fig. 3. Evolution of the ionic strength in COPECs during the ionic exchange process (top). Resulting effect of the ionic strength change on the hydration and thermal properties of COPECs (bottom).

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**ICYS-MANA Researcher** 

**Koichiro UTO** 



#### 1. Outline of Research

Human tissues are sophisticated ensembles of many distinct cell types embedded in the complex, but well-defined, structures of the extracellular matrix (ECM). Dynamic biochemical, physicochemical, and mechano-structural changes in the ECM define and regulate tissue-specific cell behaviors. To recapitulate this complex environment *in vitro*, dynamic polymer-based biomaterials have emerged as powerful tools to probe and direct active changes in cell function.<sup>1,2)</sup> As a new approach, I propose shape-memory cell culture platform that undergoes programmed changes in either "surface" topography and "bulk" dimension in a near-physiological fashion to direct cell behavior.

#### 2. Research Activities

# (1) Spatiotemporal Control of Cardiac Anisotropy Using Dynamic Nanotopographic cues.

In order to evaluate the potential for cultured cardiomyocytes to respond to dynamic changes in their in vitro microenvironments as they do in vivo, I investigated the behavior of cardiac cell sheets on nanofabricated substrates with controllable anisotropic topographies.<sup>3)</sup> A thermally induced shape-memory polymer (SMP), chemically crosslinked poly(*ɛ*-caprolactone) (PCL), was employed to assess the effects of a 90° transition in substrate pattern orientation on cardiomyocyte contractile function. Cardiac cell sheets cultured on patterned SMPs underwent reorientation of their anisotropic contraction directions in response to heat-induced transition of the underlying nanotopography. The direction of cardiomyocyte contraction reoriented by an average angle of 49 degrees, while continuing to exhibit anisotropic contractile properties (Fig. 1). These results demonstrate that initial anisotropic



Fig. 1. Alignment (top) and contraction (bottom) analysis of cardiac cell monolayer reorganization caused by an orthogonal shift in the orientation of PCL-based shape memory nanogrooves.

nanotopographic cues do not permanently determine the fate of cardiomyocyte orientation. Instead, cardiac cell sheets are capable of reorganizing their cytoskeletal structures to remain in line with altered substrate directional cues. Given the importance of matrix guidance cues in regulating primary and stem cell development, investigation of such dynamically tunable nanoscale topographies may have important implications for advancing cellular maturation and performance *in vitro*. Achievement of mature cardiac structures and functionality in engineered tissues will in turn benefit *in vitro* studies of cardiac muscle physiology and pathology, as well as having potential value in developing bioengineered therapies for treatment of myocardial infarction *in vivo*.

#### (2) Temporal Control of Cellular Alignment Using 'Bulk' and 'Surface' Shape-Memory Transitions.

I also designed novel shape-memory cell culture platform that is capable of simultaneously tuning surface topography and dimensionality to manipulate cell alignment.<sup>4)</sup> First, a shape-memory PCL with switching temperature near body temperature was successfully prepared by tailoring of nanoarchitectures. The temporary strain-fixed PCLs were prepared by processing through heating, stretching, and cooling about the switching temperature. Temporary nanowrinkles were also formed spontaneously during the strainfixing process with magnitudes that were dependent on the applied strain. The surface features completely transformed from wrinkled to smooth upon shape-memory activation over a narrow temperature range. Shape-memory activation also triggered dimensional deformation in an initial fixed strain-dependent manner. A dynamic cell-orienting study demonstrated that surface topographical changes play a dominant role in cell alignment for samples with lower fixed strain while dimensional changes play a dominant role in cell alignment for samples with higher fixed strain. Because the proposed system is simple, versatile, and biologically friendly, I believe that these findings could serve as the basis for designing the dynamic cell culture substrates for mimicking the dynamic in vivo environments with shapememory materials. In addition, the proposed shape-memory cell culture platform will become a powerful tool for further development of spatio-temporal control of mechanostructural properties of materials to direct cell fate.

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### Nanosheets of Boron-Carbon-Nitrogen System for Energy and Composite Applications ICYS-MANA Researcher Xue-Bin WANG



#### 1. Outline of Research

High-power high-energy electricity storage devices are essential for energy issues. 2D functional nanosheets of light elements in boron-carbon-nitrogen system, *e.g.* representative graphene and boron nitride (BN) nanosheets, are outstanding models of 2D nanosheets offering unique physics and exciting functionalities. Herein our research focuses on the novel syntheses of graphenes and BN nanosheets and on their applications for supercapacitors and diverse composite materials.

#### 2. Research Activities

# (1) 3D Graphene: Synthesis and High-Power-Density Supercapacitor.<sup>1,2)</sup>

3D graphenes are most desired to deliver the unique nano-sized properties of graphenes to the macro-scale, yet their practical production remains insufficient. Herein we established a general synthesis approach, *i.e.* ammonium-assisted chemical blowing *via* foaming sugars into the bubble networks of sugar-derived polymers, to effectively produce the 3D strutted graphenes (SG, Fig. 1).

SG consisted of interconnected mono-/few-layered graphene membranes scaffolded by graphitic struts without restacking or agglomeration, which thus fully exposes the huge surface and possesses appropriate porosity. The SG was further applied as additive/binder-free electrodes for supercapacitors. When compressing the SG electrodes, the thickness of active materials became *ca.* 2% of the original value with the same area. The density was estimated as 0.1 g/cm<sup>3</sup>. Although the resistance resulting from compression damage on SG networks increased, SG networks were basically kept. This contributed the 10-times increase of the maximum volumetric power density, up to 27 kW/L, which



Fig. 1. (a-c) Photos and HRTEM images of SG with strutted structures consisting of struts and graphene membranes; (d) Ragone plots of maximum volumetric power density *versus* volumetric energy density of supercapacitors based on 3D graphenes (RGO is reduced graphene oxide).

was higher than electrolyte-mediated oriented RGO hydrogel at the same packing density.

#### (2) 3D BN-nanosheet Foam: Synthesis and Composite.<sup>3-5)</sup>

We produced the large quantities of BN foams based on a similar self-chemical blowing method *via* extending the aforementioned blowing technique to BN system. It utilized a multistage heating of ammonia borane, in which a lot of released  $H_2$  gas during pyrolysis blew numerous polymer bubbles into foams of BN nanosheets. The nanosheets were further utilized for making the thermoconductive epoxy/BN composites. The composites demonstrated the14-fold increase in thermal conductivity, which was useful for the electronic packaging materials.

To further reduce the cost of BN, we used the cheap raw materials of formaldehyde, dicyandiamide and boric acid to produce BN-based porous monoliths (BNPMs), *via* a facile two-step template-free reaction including self-bubbling precursor solidification and high-temperature pyrolysis. The BNPMs exhibited the high specific surface area up to 1406 m<sup>2</sup>/g. They were applied for the highly efficient separation-adsorption purification of an oil/water system, demonstrating an excellent adsorption capacity of up to 71-98% (volume-based adsorption capacity) toward a wide selection of oil contaminants (Fig. 2).



Fig. 2. (a) Photos of a precursor monolith and BNPM. (b) XRD patterns of the precursor monolith and BNPM. (c-d) SEM images of BNPM showing the pores.

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### Robust Superconductivity of Atomic-Layer Indium under In-Plane Magnetic Fields ICYS-MANA Researcher Shunsuke YOSHIZAWA



#### 1. Outline of Research

Topological superconductivity is a novel state of matter originating from the topological nature of superconducting order parameter. Quantum vortices in a topological superconductor can host Majorana fermions, which are expected to play a key role in topological quantum computing. Our final objective is to create topological superconductivity in surface materials and detect Majorana fermions using scanning tunneling microscope (STM).

Many of the proposed models for topological superconductivity involve superconductivity induced in spin-split energy bands. Such spin splitting occurs when a crystal lacks space-inversion symmetry. Since surfaces automatically break this symmetry, starting from atomic-layer superconductors on semiconductor surfaces<sup>1)</sup> would be advantageous. Another benefit is that their surfaces are clean enough to perform detailed STM experiments.<sup>2,3)</sup> However, influences of symmetry breaking on the properties of atomic-layer superconductors have not been clarified experimentally. Currently, we are going to reveal various novel phenomena predicted to occur in superconductors without space-inversion symmetry. For this purpose, we have developed an ultra-high-vacuum (UHV) compatible cryostat for electron transport measurements.

#### 2. Research Activities

# (1) New equipment for low-temperature electron transport measurements in magnetic fields.

Fig. 1a shows a photograph of the new equipment. It is basically a sorption-pump based top-loading cryostat equipped with a superconducting solenoid magnet. It allows us to measure the resistivity of atomic-layer superconductors at temperatures down to 0.9 K and in magnetic fields up to 5 T. An important feature of this equipment is that the sample is rotated in-situ by using piezoelectric motor so that one can precisely control the angle of the magnetic fields with respect to the sample surface. Samples are prepared in an existing UHV chamber and transferred to the new



Fig. 1. (a) UHV-compatible cryostat for electrical transport measurements in magnetic fields. (b) Sample cartridge with a rotatable stage.

equipment using a portable UHV chamber. There is a UHV chamber just above the cryostat. Here, one of the samples is mounted on the piezoelectric motor fixed to the `sample cartridge' shown in Fig. 1b. The cartridge is transferred to the measurement space at the bottom of the cryostat using a long vertical transfer rod. Note that the samples are kept in UHV throughout the experiment. This is crucial for obtaining reliable data. For efficiently carrying out measurements in various modes, LabVIEW based computer programs have been written from scratch.



Fig. 2. Temperature dependence of sheet resistance of Si(111)- $(\sqrt{7} \times \sqrt{3})$ -In in magnetic fields perpendicular (a) and parallel (b) to the two-dimensional layer.

# (2) Resistivity measurements of atomic-layer indium in magnetic fields.

The performance of the new equipment have demonstrated in the resistivity measurement of Si(111)- $(\sqrt{7}\times\sqrt{3})$ -In, an atomic-layer superconductor with a critical temperature  $(T_c)$  of 3 K. Fig. 2a shows the temperature dependences of sheet resistance R<sub>sq</sub> measured in magnetic fields perpendicular to the surface. A significant suppression in  $T_{\rm c}$  is observed even in a small magnetic field of 0.02 T, and the signature of superconducting transition disappears in 0.5 T. In contrast,  $T_{\rm s}$  is far less sensitive to in-plane (parallel) magnetic fields up to 5 T. By extrapolating the in-plane-field dependece of  $T_{\rm c}$ , the upper critical field at zero temperature is estimated to be about 15 T for the present sample. This large upper critical field may be understood if the electronic bands are split due to a space-inversion symmetry breaking. This was unexpected, as the previous reports of angle-resolved photoemission on Si(111)-( $\sqrt{7} \times \sqrt{3}$ )-In with moderate energy resolution (15-50 meV) show no signature of such splitting. Possible small band splitting that could not be detected by photoemission might be responsible for the observed robustness of the superconductivity.

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