MANA
Progress Report

Research Digest 2013

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 founded in 2007 as one of the original five centers under the World Premier International Research Center (WPI) Initiative of Japan's Ministry of Education, Culture, Sports, Science and Technology (MEXT). Winning critical acclaim for the research achievements in its first five year term, MANA advanced into its second term in 2012. Our vision is to "create a better future for humanity by opening up a new paradigm of nanotechnology through supporting the development of new materials." MANA believes that conceptual innovation must be brought into the nanotechnology developed to date. We express the concept of this innovated nanotechnology by the term nanoarchitectonics, making effective use of it in everyday research activities in search for new materials.

MANA achieved outstanding research results in its first term five year term not just because we steered ourselves in the unique research direction stated above but also because we have been dedicated to building an international environment. Around half of our researchers come from overseas, we train young scientists, promote interdisciplinary research and send research outcomes out to the world. MANA will continue to be committed to researching new materials as a world leading institute, and I am looking forward to your warm support for our activities.

The MANA Progress Report consists of two booklets named "Research Digest 2013" and "Facts and Achievements 2013". This booklet "Research Digest 2013" presents MANA research activities and the other booklet "Facts and Achievements 2013" serves as a summary to highlight the progress of the MANA project.

Nano Revolution
for the Future

MANA Research Digest 2013

MANA Principal Investigators (22) and Associate Principal Investigators (2)

Nano-Materials Field

Nano-System Field

Nano-Power Field

Nano-Life Field

Group Leaders (11)

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ICYS-MANA Researchers (10)

Inorganic Nanosheets

MANA Principal Investigator **Takayoshi SASAKI**
(Field Coordinator)
MANA Scientist Yasuo Ebina, Renzhi Ma, Tadashi Ozawa, Nobuyuki Sakai
MANA Research Associate Baowen Li, Tosapol Maluangnont, Fengxia Geng,
Chengxiang Wang, Jianghua Wu
Graduate Student Yasuhiro Aoyama, Xingke Cai, Lei Dong

1. Outline of Research

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

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

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

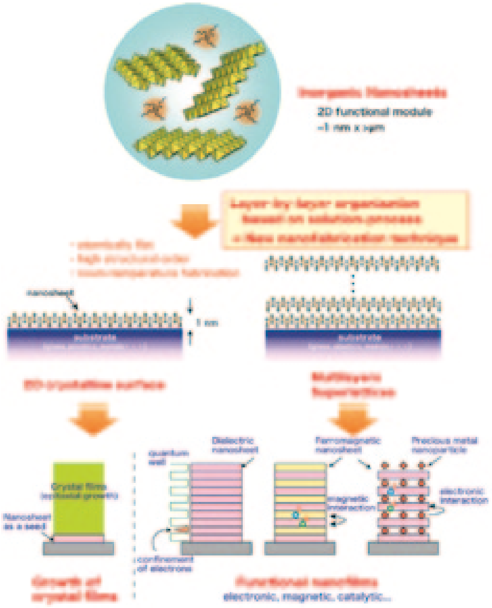

Fig. 1. Conceptual explanation of the research plan.

2. Research Activities

(1) Massive Swelling Behaviors of Layered Titanates.[1)]

We found that platy microcrystals of a layered titanate underwent huge degrees of swelling in aqueous aminoalcohol solutions. The crystals a few micrometer thick elongated into string-like objects over 200 μm long within a few seconds when brought into contact with the solution (Fig. 2), and mostly returned back to original size and shape also in seconds. SAXS measurements revealed that the interlayer galleries evenly expanded to several tens nanometers. A maximum swelling of 90 nm is ~100 folds expansion with respect to the original value. It is to be noted that the crystals showed this enormous swelling/shrinkage without broken into smaller segments, which is very different from behaviors in solutions of quaternary ammonium ions as a delaminating agent. First principles calculation results suggest the evolution of a directionally ordered network of water molecules around the aminoalcohol molecule, which may be a key for the unusually stable swelling without delamination.

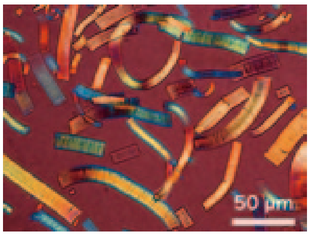

Fig. 2. Optical image of titanate crystals highly swollen in an aminoalcohol solution.

(2) The nanosheet seed layer to control the oriented growth of functional crystal films.[2)]

We succeeded in controlled oriented growth of $SrTiO_3$ films on a glass substrate covered with suitable nanosheets as a seed layer. Selection of oxide nanosheets such as $Ca_2Nb_3O_{10}^-$, $Ti_{0.87}O_2^{0.52-}$, and $MoO_2^{\delta-}$ led to tune (100), (110) and (111) orientations (Fig. 3), respectively, based on their structural similarities to corresponding crystallographic planes of the perovskite structure. Dangling bond free nature of the nanosheets promotes van der Waals epitaxy-like growth, allowing some structural mismatch.

Fig. 3. Cross-sectional TEM images of oriented $SrTiO_3$ films grown on a glass substrate covered with suitable nanosheets.

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Supramolecular Materials

MANA Principal Investigator **Katsuhiko ARIGA**
MANA Scientist Jonathan P. Hill, Qingmin Ji, Lok Kumar Shrestha, Waka Nakanishi
MANA Research Associate Jan Labuta, Tatyana Terentyeva, Pathik Sahoo

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.[1-7]

2. Research Activities

(1) Mesoporous Fullerene Crystal.[1)]

A new class of fullerene (C_{60}) crystals with bimodal pore architectures consisting of macropores and mesopores was synthesized by using a liquid-liquid interfacial precipitation (LLIP) method involving an interface between isopropyl alcohol (IPA) and a saturated solution of C_{60} in a mixture of benzene and carbon tetrachloride (CCl_4, Fig. 1). By varying the mixing fraction of CCl_4 in benzene, the porosity and electrochemically active surface area can be flexibly controlled.

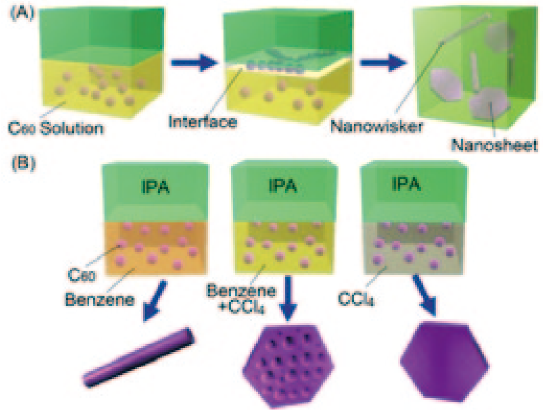

Fig. 1. (A) Synthetic routes of fullerene (C_{60}) crystallization using a liquid-liquid interfacial precipitation (LLIP) method. (B) Preparation of C_{60} crystals with various shapes.

(2) NMR Detection of Chirality using Achiral Indicator.[2)]

We reported an effective method of enantiomeric excess determination using a symmetrical achiral molecule as resolving agent, which is based on complexation with analyte (in fast exchange regime) without formation of diastereomers (Fig. 2). The use of *N,N'*-disubstituted oxoporphyrinogen as resolving agent makes this novel method extremely versatile being available for various chiral analytes including carboxylic acids, esters, alcohols and protected amino acids using the same achiral molecule. The model of sensing mechanism exhibits a fundamental linear response between enantiomeric excess and observed magnitude of induced chemical shift non-equivalence in ^{1}H NMR spectra.

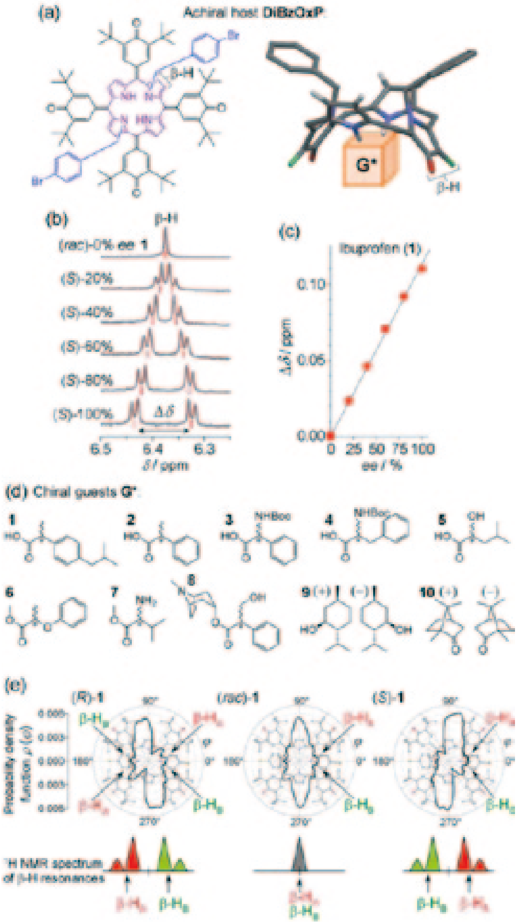

Fig. 2. (a) Chemical structure of DiB$_z$O$_x$P and scheme of 1:1 host-guest complex formation. (b) Partial ^{1}H NMR spectra of pyrrolic β-H (reporter group) resonances of DiBzOxP in presence of various *ee* of chiral guest 1 (ibuprofen). Note well-resolved narrow resonances. (c) Linear relationship between ee of 1 and induced chemical shift non-equivalency Δ*δ* as obtained from (b). (c) List of various chiral guests that can be utilized for sensing (all show linear response to *ee*). (e) Plot of probability function ("chiral field") as obtained from classical molecular dynamics simulations for DiB$_z$O$_x$P and 1 complex. Influence of "chiral field" on pyrrolic β-H part of ^{1}H NMR spectra is shown.

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Inorganic Nanostructured Materials

MANA Principal Investigator **Yoshio Bando**
(MANA Chief Operating Officer)
MANA Scientist Ryutaro Souda, Yusuke Ide
MANA Research Associate Xuebin Wang, Jun Zhang, Nethravathi Chikkavenkataswamy
Graduate Student Wei Tian, Dequan Liu

1. Outline of Research

Our ultimate goal is to explore novel inorganic nanostructured materials such as nanosheets, nanowires, nanotubes, and nanoparticles, as well as their unique physics and chemistry deriving from their small size down below a critical scale. In order to accomplish this purpose, we set up a full set of instruments for syntheses and characterizations of nanomaterials, such as induction furnace, electrospinning, electrochemical workshop and transmission electron microscope *etc.*; these enable the effective control of the syntheses, and the further investigation of their energy storage capability and optics detector performance for applications in energy storage and ultra-violet detection *etc*.

2. Research Activities

(1) Strutted-Graphene: New-Style 3D Graphene for High-Power-Density Supercapacitors.[1)]

Inspired by an ancient food art of “blown sugar”, we develop a “sugar blowing” technique (Fig. 1) to grow a new-style 3D self-supported graphene product, named by us as strutted-graphene (SG). SG consists of continuous graphitic membranes which are homogenously connected and spatially supported by the networks of micrometer-width graphitic struts. The high electrical conductivity, specific surface area, mechanical strength and elasticity are thus simultaneously achieved in this SG. And the featured facile low-cost high-throughput production combining their unique product properties enables immediate practical applications, *e.g.* the highlighted highest power-density of electrochemical capacitors (893 kW/kg) as demonstrated by us. The SG is also envisaged as effective support, catalyst, sorbent, hydrogen reservoir, gas sensor, air filter and sound absorber.

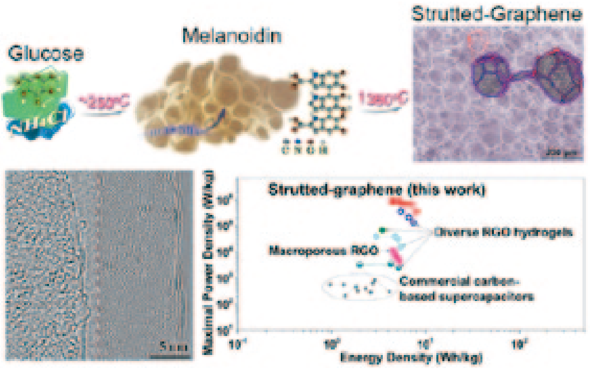

Fig. 1. (Top) Sugar-blowing process for growing strutted-graphenes; (bottom) HRTEM images of two few-layered graphene membranes, and a survey of maximum power density vs. energy density of aqueous EDL-type supercapacitors based on diverse 3D graphenes (RGO = reduced graphene oxide).

(2) Boron Nitride Porous Microbelts for Hydrogen Storage.[2)]

A novel BN material, *i.e.* porous microbelts, is achieved by a template-free reaction (Fig. 2). The easily operable production is conducted by heating a boron acid - melamine precursor in ammonia at 1100°C. More than turbostratic structures and developed pore channels, BN porous microbelts demonstrate a highest specific surface area up to 1488 m^2/g among reported BN materials. They thus exhibit decent and reversible hydrogen uptakes of 2.3 wt%, due to the unique pore structures and high surface area. This promotes commercially applicable H_2 storage materials.

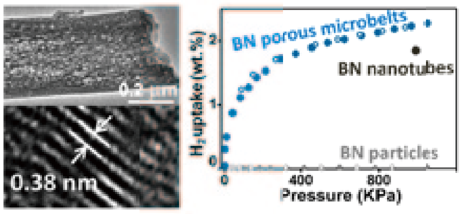

Fig. 2. (Left) TEM and HRTEM images of BN porous microbelts with a (0002) spacing identified to hexagonal BN. (Right) Hydrogen adsorption-desorption isotherms of BN at 77 K.

(3) Electrospun ZnO-SnO$_2$ Nanofibers for Fully Transparent Ultraviolet Photodetectors.[3)]

We successfully fabricated an ideal fully transparent film constructed of ZnO-SnO$_2$ heterojunction nanofibers *via* a facile electrospinning method (Fig. 3). The photodetectors are then fabricated by depositing two electrodes, which can be easily scaled up at a low cost while requiring no any lithography-based assembly. The transparent devices show excellent operating characteristics: high ultraviolet sensitivity and photo-dark current ratio of 4600 (5 times more than previous reports), and fast response time of 32 s against typically previous 100 s; this suggests their great potentials for applications in transparent electronics and high-performance photodetectors.

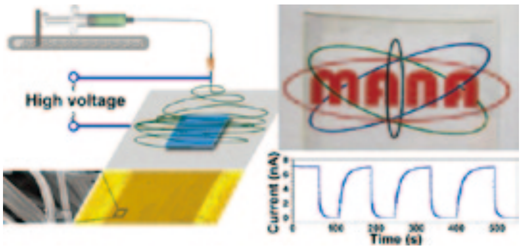

Fig. 3. (Left) Schematic diagram illustrating electrospinning fabrication of ZnO-SnO$_2$ nanofibers and images of fabricated films with two ITO electrodes (two bright parts). (Right) Transparent photodetector and its response to a 300-nm light.

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Nano Electrics and Related Materials

MANA Principal Investigator **Toyohiro CHIKYOW**
MANA Scientist
Masahiro Goto, Yutaka Wakayama, Jin Kawakita,
Takahiro Nagata, Takayuki Nakane, Shinjoro Yagyu,
Michiko Yoshitake, Yoshiyuki Yamashita

1. Outline of Research

In the future large scale integrated circuit (LSI), due to the scaling of the transistors, new materials exploration and atomically controlled nano interfaces are required to realize smaller devices.[1] From the past to present, Si has been used as the substrate for device and to improve the device performance and achieve the scaling, "high-k" materials such as La_2O_3 or HfO_2 have been extensively studied.[2] However, due to the interface trap or fixed charge in high-k oxide, the carrier mobility was reduced. To enhance the mobility for higher speed switching, alternative substrates are considered. One candidate is Ge substrate, because Ge has a higher carrier mobility compared to Si. However, thermally grown GeO_2 has many defects in the film and does not work well as the gate insulator. To improve the quality of the GeO_2, high pressure oxidation and other methods have been attempted, though the solution is not obtained yet.[3]

One solution is to find another gate oxide material for Ge substrate. Also in the selection, future scaling must be taken into account. This means that the material should have a direct contact to Ge with less interface defects and electrically active traps.

2. Research Activities

(1) Materials design of gate insulator for Ge.

To obtain a direct contact of oxide to Ge, the first step is to select a new material. A similar approach was demonstrated for materials on Si. The criteria for the reaction is heat of formation.[4,5] GeO_2 has 114 Kcal/mole. Therefore the practical bonding energy is 57 Kcal/bond, because GeO_2 has two bondings.

TiO_2 is known to have a higher dielectric property and the heat of formation is 225.9 Kcal/mole, which means each bonding energy is 112.9 Kcal/bond. This value is almost half of GeO_2 heat of bonding. This estimation means that if the oxygen deficient TiO_x has a contact with GeO_2, the TiO_2 is formed by GeO_2 reduction, and the GeO_2 layer is eliminated if the thickness is so thin that all oxygen is consumed.

(2) New gate stack structure of HfO_2/TiO_2/Ge.

After the degreasing and surface cleaning by HF solution, a Ge substrate was installed in the vacuum chamber, where pulsed laser deposition (PLD) was done for TiO_2 and HfO_2 deposition. This system was equipped with Reflection of High Energy Electron Diffraction (RHEED) to investigate surface reconstruction. After annealing at 500 degree Celsius, the RHEED pattern showed clear 2x1 reconstructed structure, meaning that the surface of Ge was clean and showed atomically flat surface.

Subsequently, TiO_2 was deposited on the surface by PLD in oxygen atmosphere of 10^{-6} Torr. Surprisingly, in the growth of oxygen atmosphere, epitaxial growth of TiO_2 was observed. These results showed that TiO_2 grew selectively and though GeO_2 was formed, it was decomposed and reduced.

X-ray diffraction after the TiO_2 deposition showed an epitaxial growth of Rutile TiO_2. Also by XPS, interfacial layer of GeO_2 was not observed and abrupt interface of TiO_2/Ge was demonstrated.

Then HfO_2 was deposited on the TiO_2 to fabricate gate stack structure, followed by Pt deposition. The MOS capacitor structure is shown in Fig. 1. C-V did not show a hysteresis, meaning that fixed charge or interface trap density was not so high. At the same time, the equivalent oxide thickness (EOT) to SiO_2 was estimated to be 0.78 nm. This value was the smallest value of high-k insulator on Ge.

In summary, a new gate insulator stack of HfO_2/TiO_2 was proposed for Ge substrate. Materials design was done based on thermodynamics. TiO_2/Ge interface was abrupt and preferable materials of HfO_2/TiO_2 was selected. EOT of was HfO_2/TiO_2 was estimated to be 0.78 nm, which is the smallest EOT on Ge. From the results, HfO_2/TiO_2 stacked oxide was found to be the best materials for Ge MOSFET.

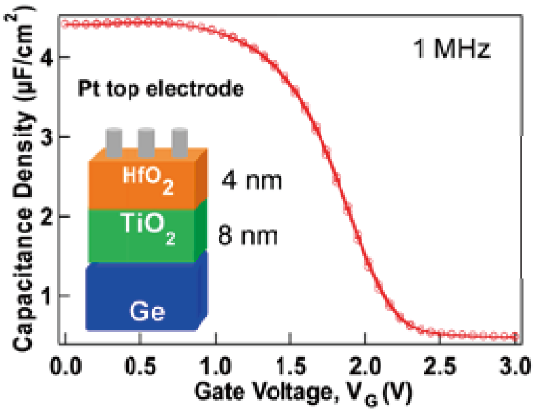

Fig. 1. MOS capacitor structure for HfO_2/TiO_2/Ge. The C-V characterization showed less hysteresis and estimated EOT was 0.78 nm.

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Nano-Dichalcogenide Properties Studied by *In-Situ* TEM

MANA Principal Investigator	**Dmitri GOLBERG**
MANA Scientist	Masanori Mitome, Naoyuki Kawamoto
MANA Research Associate	Amir Pakdel, Xia Li, Zhi Xu
ICYS-MANA Researcher	Daiming Tang
Graduate Student	Maho Yamaguchi, Qunhong Weng, Chao Zhang

1. Outline of Research

Nanostructured dichalcogenides, like nanotubes, nanosheets and nanoribbons of MoS_2, WS_2 and other inorganic compounds, are expected to greatly contribute to the Nano-Materials Field of the 21st century. In theory, due to the existing semiconducting band-gaps, which are not available in a standard C graphene, they may effectively serve as novel miniaturized field-effect transistors or other smart electronic components in the future nanoelectronic schemes and devices. However, in practice, their *nano*-properties have rarely been experimentally accessed due to tiny lateral dimensions and non-availability of reliable experimental setups for analyzing electrical and mechanical performance at such ultimately downsized scales. The state-of-the-art microscopic facilities developed by the Nanotubes Group of MANA, *i.e.* atomic force microscope (AFM) and scanning tunneling microscope (STM) units combined with a high-resolution transmission electron instrument (HRTEM), allows us to precisely and *in situ* measure the strength, elasticity and conductance of any individual dichalcogenide nanostructure on the individual structure level and at the highest spatial, energy and temporal resolutions.

2. Research Activities

(1) Tensile strength of individual WS_2 nanotubes.

Deformation and fracture mechanisms of multiwalled WS_2 nanotubes (NTs), with external diameters up to 60 nm, under tension were for the first time analyzed in HRTEM, Fig. 1.[1)] NTs deformed elastically until abrupt brittle fracture. In average, the tensile strength reached at ~10 GPa. Specific deformation feature was an effective intershell cross-linking. This phenomenon allows the tubes to withstand very high loadings, up to ~3000 nN, *i.e.* much higher values than those peculiar to the well-structured non-cross-linked WS_2 tubes reported previously.

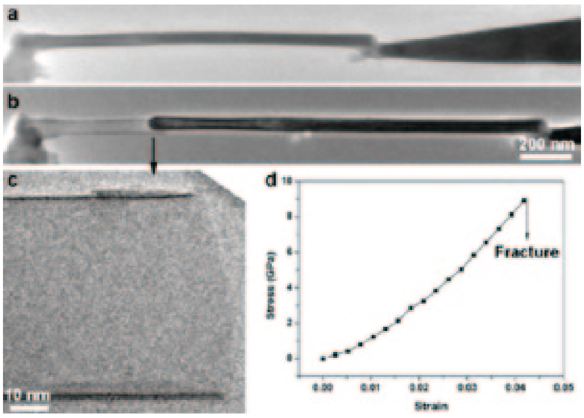

Fig. 1. (a, b, c) Tensile test on a WS_2 nanotube with the outer 3 shells fractured at once. (d) A corresponding stress-strain curve recorded.

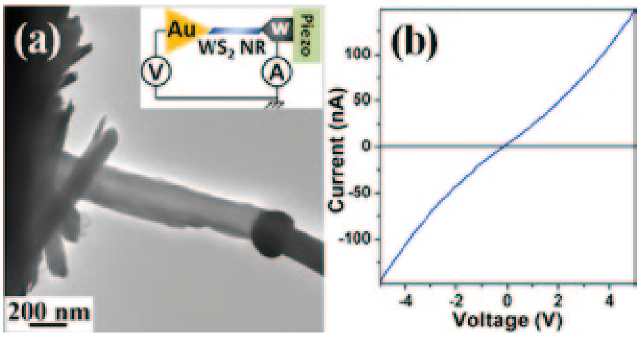

Fig. 2. TEM image showing the experimental set-up inside TEM for measuring WS_2 nanoribbon conductance (a) and corresponding *I-V* curve recorded on an individual WS_2 nanoribbon (b).

(2) Electrical properties of individual WS_2 nanoribbons.

Free-standing WS_2 nanoribbons (NR) were for the first time prepared *via* chemical unzipping of WS_2 NTs under lithiation and consequent reaction with thiol molecules.[2)] Opposed to the starting high-resistant semiconducting WS_2 nanotubes, the nanosheets (after tube unwrapping) revealed conducting behavior with a resistance of 40 MΩ, Fig. 2. This result goes in line with the comparable theoretical calculations of the starting WS_2 nanotubes and nanoribbon band structures performed by us.[3)]

In Fig. 3 both double- and singlewalled WS_2 nanotubes display semiconducting properties with indirect band gaps of 0.9 eV and 1.55 eV, respectively, while the unzipped WS_2 nanoribbon exhibits a metallic character.

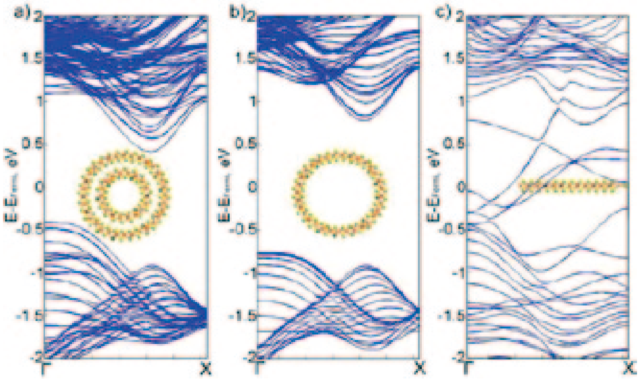

Fig. 3. Band structure of a) (9,9)@(16,16) WS_2 NT, b) (16,16) WS_2 NT and c) WS_2 NR. The Fermi level energy is taken as zero.

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Nanogenerators as a New Energy Technology

MANA Principal Investigator **Zhong Lin WANG**
(Satellite at Georgia Tech, USA)
Research Scientist Guang Zhu
Graduate Student Sihong Wang

1. Outline of Research

In the last half century, the developing trend of electronics is miniaturization and portability. The history of computers is a typical example, from the vacuum tube based huge-size machine, to solid state MOSFET based main frame computer and later laptop computer, and now to handhold cell phone; the number of such computers the world possess changed from a few worldwide, to one per unit, and now one per person. The near future development is about the electronics that are much smaller than the size of a cell phone, so that each person can have at least dozens to hundreds of such small electronics on average. Such a small size electronics and its working mode like a sensor largely reduces its power consumption, making it possible to use the energy harvested from our living environment to power it. It will become impractical if sensor networks has to be powered entirely by batteries because of the huge number of devices, large scope of distribution, and difficulty to track and recycle to minimize environmental impact and possibly health hazardous.

We have been developing an area of nanoenergy, aiming at using nanotechnology to harvest the energy required for sustainable, independent and maintenance free operation of micro/nano-systems and mobile/portable electronics. As first reported in 2006, various nanogenerators (NGs) have been demonstrated using piezoelectric, triboelectric and pyroelectric effects (Fig. 1). These technologies were first invented at Georgia Tech and we are the world leader in the field with unique characteristics. By using the energy from our living environment, our goal is to make self-powered system. As of now, we have demonstrated various applications of using the NG technology for powering various mobile electronics, making it possible that the NG will reach our life very soon. We have also developed various hybrid cell technologies for simultaneously harvesting multi-type energy so that we can use all of the available energy in the environment where the devices are being deployed. Lastly, integrated self-charging power cell provides an innovative approach for hybridizing nanogenerator with energy storage unit in a convoluted process. The self-powering approaches developed here are a new paradigm in nanotechnology and green energy for truly achieving sustainable self-sufficient micro/nano-systems, which are of critical importance for sensing, medical science, infrastructure/environmental monitoring, defense technology and personal electronics.

2. Research Activities

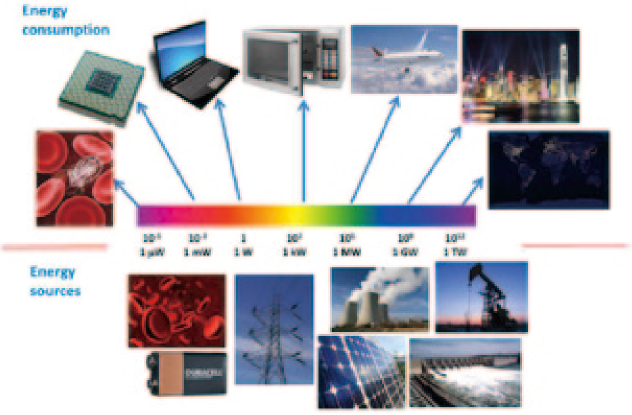

Fig. 1. The scale in power. The right-hand side is the large-scale energy needs. The ones at the left-hand side is the field of nanoenergy for portable electronics, which is the focus of our current research.

We have recently invented the triboelectric NG at Georgia Tech for generating electricity by utilizing the triboelectric effect.[1] The triboelectric effect is a type of contact charging effect in which certain materials become electrically charged after they come into contact with other materials. According to a material's tendency to gain or lose electrons upon contact with other materials, a triboelectric series is formulated. Such an effect is usually regarded as an annoying or even hazardous phenomenon because it may lead to ignition, dust attraction, and damage to electronics. Very few efforts have been made to utilize this effect in energy harvesting. Recently, we demonstrated a miniaturized triboelectric NG with low cost and easy fabrication. Owing to the coupling of contact charging and electrostatic induction, electric generation was achieved with repeating contact between two polymer films that differ in polarity in triboelectric series. The instantaneous electric power density reached as high as 300 W/m^2 and 400 kW/m^3. Triboelectric NG has been demonstrated as an effective means for harvesting wind energy, motion/vibration energy and even ocean wave energy.

A self-powered nanosystem is that it can operate wirelessly, independently and sustainably. The goal of this proposal is to develop the self-powering as a new paradigm in nanotechnology for truly achieving sustainable self-sufficient micro/nano-systems, which are of critical importance for sensing, medical science, infrastructure/environmental monitoring, defense technology and even personal electronics. We anticipate seeing that nanogenerator will play a key role for driving small electronics in a few years.

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Nanosheet Electronics

Associate Principal Investigator Minoru OSADA

1. Outline of Research

Recent advances in delamination techniques have produced 2D nanosheets of various materials including graphene, metal oxides, boron nitride, and metal disulfides. These 2D nanosheets are now considered to be excellent candidates for future electronic applications. Graphene is one of the most promising materials being researched today due to many amazing functionalities such as high electron mobility and quantum Hall effects. Isolated just 9 years ago, graphene has extraordinary physical properties, prompting researchers to suggest that graphene will one day replace silicon in electronic devices. However, graphene is a conductor, and electronic technology also requires semiconductors and insulators. Along with graphene, 2D nanosheets of other layered materials have increasingly attracted fundamental research interest because of their potential to be used as insulators, semiconductors, and even conductors. Oxide nanosheets may be the perfect solution as a new era unfolds in the development of 2D nanosheets. Currently, using solution-based exfoliation techniques, it is possible to investigate dozens of different oxide nanosheets in the search for new phenomena and applications.

We are working on the creation of new 2D oxide nanosheets and the exploration of their novel functionalities in electronic applications. Our particular focus is on establishing nanoarchitectonics of 2D oxide nanosheets through finely controlled synthesis, hierarchical structural assembly, and device design (Fig. 1).

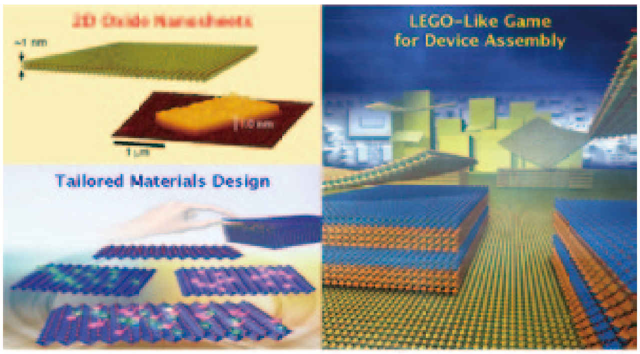

Fig. 1. General outline of our research.

2. Research Activities

Oxide nanosheets have distinct differences and advantages compared with graphene because of their potential to be used as insulators, semiconductors and even conductors, depending on their chemical composition and structures. There is enormous interest in building devices and functional materials based on 2D oxide nanosheets of different compositions to complement those from graphene. We found that perovskite-based nanosheets exhibit superior high-κ performance ($\varepsilon_r > 300$) even at a few-nm thicknesses, essential for next-generation electronics. Additionally, nanosheet-based high-κ capacitors exceeded textbook limits, opening a route to new capacitors and energy storage devices.1) These topics are an important target for “More & Beyond Moore” technology promoted by the International Technology Roadmap for Semiconductors.

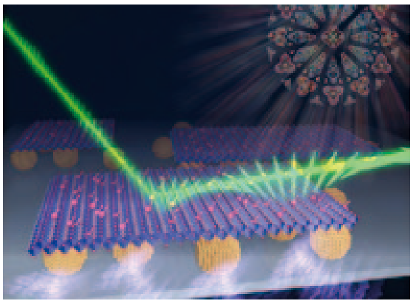

Fig. 2. New magneto-plasmonic nanoarchitectures consisting of 1-nm thick ferromagnetic nanosheets and Au nanoparticles.

Our current projected research is directed towards the construction of 2D nanoarchitecture systems, which allow the artificial design of new functionalities and nanodevices through solution-based nanotechnology. We utilized oxide nanosheets as a building block in the LEGO-like bottom-up fabrication, and successfully developed innovative multifunctions in 2D nanoarchitecture systems through control over the cooperative interaction of organized components. One enticing possibility is the hetero-assembly of conducting/high-*k* nanosheets.2) Such a superlattice allows the rational design of high-performance FET devices, which realize mobility enhancement by dielectric screening. Other important and attractive topics include: (i) lead-free high-T_C ferroelectrics,3) (ii) metamaterials with unusual optical responses, and (iii) plasmonic sensors using ferromagnetic nanosheets/Au (Fig. 2).4) In particular, the magneto-plasmonic nanosystem (Fig. 2) with a gigantic magneto-optical activity is appealing for new applications in all-optical magnetic data storage and nano-sensing. Our work is a proof-of-concept, showing that new functionalities and nanodevices can be made from 2D nanoarchitectures.

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Nano-System Architectonics

MANA Principal Investigator **Masakazu AONO**
(MANA Director-General, Field Coordinator)
MANA Scientist Yuji Okawa, Makoto Sakurai, Hideo Arakawa, Masanori Kono
MANA Research Associate Marina Makarova, Koley Pradyot

1. Outline of Research

The goal of our Nano-System Organization Group is to create new nano-systems with novel functionality by the use of various key technologies of "materials nanoarchitectonics" and put the created nano-systems to practical use to contribute to our society in such forms as next-generation information processing and communication and environmental and energy sustainability. To achieve this interdisciplinary research, we make close collaboration with other research groups in MANA. We are also making collaboration with MANA's satellite labs headed by Prof. James Gimzewski (UCLA, USA) and Prof. Christian Joachim (CEMES-CNRS, France).

2. Research Activities

Our research activities are classified into four subjects:

1) Novel nanochemical control: For example, controlled chain polymerization for the formation of electrically conductive polymer chains at designated positions and its application to wire single functional molecules with firm "chemical soldering" aiming at the realization of single-molecule electronics.
2) New functionality by organic integration and mutual linkage of individual nanostructures, using single-crystal oxides, oxide core/shell structures, and self-organized organic materials.
3) Development of novel SPMs for nanoscale magnetic imaging without using a magnetic probe.
4) Theoretical studies of strongly-correlated electron system: For example, the essential understanding of Mott transition and high temperature superconductivity.

In the following, subject 1) will be discussed in more detail.

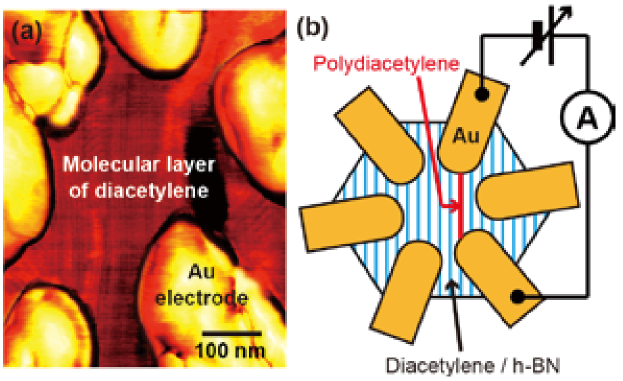

Fig. 1. (a) AFM image of diacetylene molecular layer between gold electrodes on a hexagonal boron nitride (h-BN) surface. (b) Scheme for the electrical measurements of polydiacetylene.

In order to fabricate a practical single-molecule integrated circuit, we have to develop a viable method for wiring each functional molecule. For this, a novel method for connecting single conductive polydiacetylene chains to single organic molecules was recently developed, which we named "chemical soldering". This method uses the nanoscale control of chain polymerization of diacetylene compounds in a self-assembled monolayer (SAM) on a substrate. The next step of our study is to measure the electric properties of such systems, and demonstrate the functions as a component of future single-molecule electronics. For this purpose, we found that hexagonal boron nitride (h-BN) is a promising insulating substrate for the electrical studies. We found that diacetylene molecules are able to form a flat-lying SAM on a h-BN(0001) surface. We also succeeded in fabricating gold electrodes on h-BN substrates by electron beam lithography. The formation of diacetylene SAM between the electrodes was clearly observed in the phase shift AFM image (Fig. 1a). This will enable the electrical measurements of single polydiacetylene chains and single-molecule devices (Fig. 1b).

During the above studies, we also found the formation of self-assembled arrays of gold nanoparticles on SAMs of diacetylene compounds (Fig. 2).[1] This observation confirms the role of unsaturated π systems in molecules acting as a template for the regular arrangement of gold nanoparticles, which is important for nanoelectronic and nanophotonic applications.

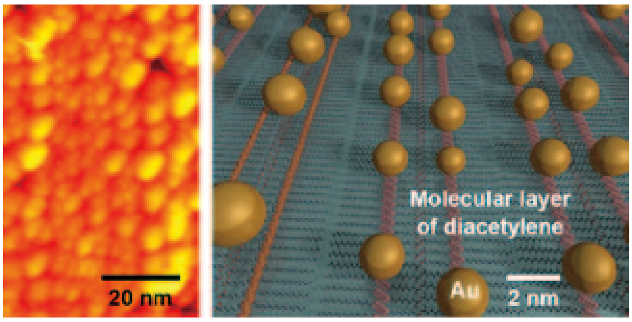

Fig. 2. STM image (left) and schematic model (right) of self-assembled arrays of gold nanoparticles on a molecular layer of diacetylene compound.

Related Publications in 2013

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2) S. Uji, K. Kodama, K. Sugii, T. Yamaguchi, T. Terashima, N. Kurita, S. Tsuchiya, M. Kohno, M. Kimata, K. Yamamoto, K. Yakushi, *Phys. Rev. Lett.* **110**, 196602 (2013).

MANA Brain: Neuromorphic Atomic Switch Networks

MANA Principal Investigator **James K. GIMZEWSKI**
(Satellite at UCLA, USA)
MANA Scientific Advisor Adam Z. Stieg
Postdoctoral Scholars Hsien-Hang Shieh
Graduate Student Researchers Renato Aguilera, Audrius Avizienis, Henry Sillin

1. Outline of Research

We have set out to develop purpose-built dynamical systems as physical platforms for modeling cortical dynamics and implementing emerging paradigms in neuromorphic computing. By leveraging the advantages of structural control with those of self-organization through a nanoarchitectonic approach,1) massively interconnected networks containing functional atomic switch elements at a density of ~10^8 synthetic synapses/ cm^2 have been produced. These atomic switch networks (ASN) have structural characteristics similar to synaptically rich connectivity matrix of the neocortex, emulate many relevant features of biological neural networks, and provide a means to explore the dynamical systems approach to a new paradigm in computation known as reservoir computing.

2. Research Activities

A merger of numerical modeling with experiment has facilitated examinations into the operational properties of ASN devices and their potential utility as a model system for hardware-based reservoir computing.

(1) Modeling and Simulation.

Modification and validation of a new operational state equation for atomic switches operation have enabled investigations of operational dependencies on physical parameters as well as explorations into the consequences of embedding atomic switches in a network setting. Validation of the numerical model and its extension to network architectures facilitated a synergy between experiment and theory in characterizing device operation and task performance.2)

(2) Next-generation Devices.

Improvements in real-time, multichannel measurement capacity have produced dramatic progress in our ability to both stimulate and interrogate ASN devices. As a result, their functional topology has been shown to produce a diversity of complex behaviors, ranging from distributed memory functions to emergent critical dynamics similar to that found in both MRI/EEG of biological brains and multi-electrode array (MEA) studies of neuronal populations.

(3) Neuromorphic Reservoir Computing.

Attempts to exploit the dynamical properties of ASNs have demonstrated a capacity to utilize controlled network plasticity and 'fading memory' property of the learned state toward applications of reservoir computing. The utility of ASNs as nonlinear reservoirs capable of task performance in the RC paradigm has been further explored through implementation of the well-known T-maze task described in Fig. 1.

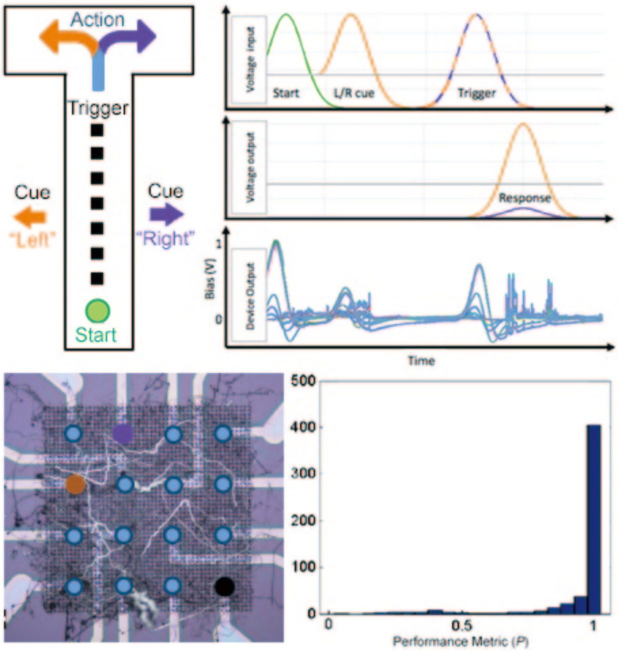

Fig. 1. (top) Schematic of the T-maze task alongside a representative sequence of start, cue, and trigger signals delivered to the ASN device during implementation. (bottom) Graphical overlay electrode channel assignments and performance for 500 runs of the T-maze task, where over 93% of L/R decisions were correct.

This delayed choice task involves a cue and trigger signal delivered to the ASN, where the cue represents a signal representing 'left' or 'right' that must be remembered and acted upon following the receipt of a subsequent trigger signal. Successful performance of the T-maze task revealed an ability to integrate, segregate, store and respond to external stimulus, these successful implementations indicate great promise for future application of the ASN as a physical platform for RC. Of particular interest are the speed, density, and scalability of the ASN, which in concert serve to overcome major hurdles in the RC paradigm.

Selected Publications with MANA recognition

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Atomic Electronics for Future Computing

MANA Principal Investigator **Tsuyoshi HASEGAWA**
MANA Scientist Kazuya Terabe, Tohru Tsuruoka
MANA Research Associate Takami Hino, Soumya R. Mohapatra, Qi Wang, Arramel, Song-Ju Kim

1. Outline of Research

We aim to explore new nanosystems showing novel functions based on atomic electronics. The new nanosystems are expected to realize new computing systems such as by achieving fault tolerant logic circuits, nonvolatile logic circuits, optical and chemical sensors, and so on. Since the present-day semiconductor systems based on CMOS devices is approaching to their maximum performance due to the ultimate downsizing, new types of logic systems using beyond-CMOS devices should be developed for further progress in information technology.

In this study, we will use the atomic electronic device, which has been developed by ourselves, for making new nanosystems. The atomic electronic device, such as atomic switch, is operated by controlling movements of cations and/or atoms in a nano-scale using nanoionics phenomena.

In order to accomplish the purpose, we will conduct 1) basic research on nanoionic phenomena, 2) developing new atomic electronics devices showing the novel functions based on the basic research, 3) developing nanofabrication technique for making the atomic electronics devices, 4) demonstration of novel operation of the atomic electronics devices and basic circuits using them.

2. Research Activities

(1) New Functions in Atomic Switches.

Volatile and nonvolatile selective switching device is one of the key elements in configuring neuromorphic systems, especially such as for achieving a recollection in memorization. We successfully achieved the volatile and nonvolatile selective operation utilizing a photo-assisted atomic switch,[1] which is a two-terminal device having a photoconductive molecular layer between two electrodes.[2]

First, the photo-assisted atomic switch was initialized with a small bias application with light-irradiation. In the initialization, an Ag whisker is grown in the photoconductive molecular layer to make a gap between the Ag whisker and a counter electrode small (about 1 nm), in which a tunneling current can flow. After the initialization, growth and shrinkage of an Ag whisker can be controlled by a bias application without light-irradiation. While an Ag whisker does not reach to the counter electrode even with the bias application, the device shows the volatile operation. When an Ag whisker reaches to the counter electrode by the bias application, the operation mode switches to nonvolatile (Fig. 1).

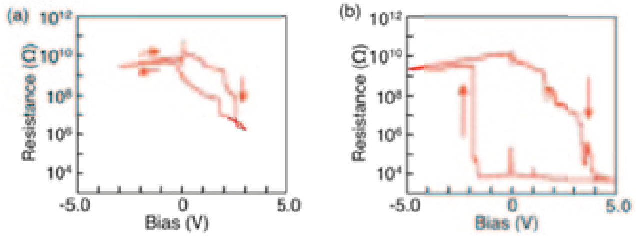

Fig. 1. (a) Volatile and (b) nonvolatile selective operations depending on a bias range, using a photo-assisted atomic switch.

We also achieved a three-terminal operation controlling an oxygen vacancy drift to cause Redox reaction at a channel region.[3] Since the device shows both n-type and p-type nonvolatile operations,[4] it has a potential to develop an electrochemical CMOS that will drastically reduce energy consumption in computing.

(2) Basic Researches on Nanoionic Phenomena.

We investigated rate-limiting processes in the fast SET operation of a gapless-type atomic switch.[5] The SET time decreased exponentially with increasing pulse amplitude, reaching as low as 1 ns using moderate pulse voltages (Fig. 2). This observation shows that oxide-based atomic switches hold potential for fast-switching memory applications. From a comparison with atomistic nucleation theory, Cu nucleation on the Pt electrode was found to be the likely rate-limiting process determining the SET time.

The basic research performed in collaboration with a group of RWTH Aachen clearly revealed a role of electromotive force in cation-based resistive switching devices.[5] These basic researches enabled the development of new functions such as synaptic functions.[6]

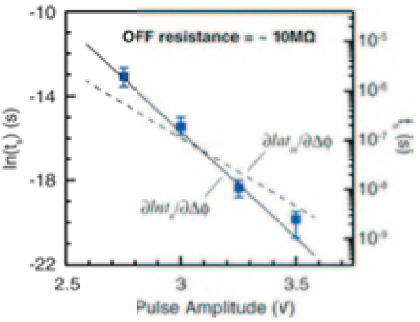

Fig. 2. SET time of Cu/Ta_2O_5/Pt gapless-type atomic switch plotted as a function of the pulse amplitude.

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Theory and Material Design for Novel Topological Insulators

MANA Principal Investigator **Xiao HU**
MANA Research Associate Takuto Kawakami, Xue Yuan Hu, Rui Yu
NIMS Postdoctoral Scientist Madhav Prasad Ghimire, Bin Xi
Graduate Student Yuki Takahashi, Feng Liu, Zhao Huang, Long-Hua Wu

1. Outline of Research

The discovery of quantum Hall effect (QHE) by von Klitzing opened a new chapter in condensed matter physics. It was revealed that the integer coefficient in Hall conductance is nothing but the Chern number which describes the topology of Bloch electronic wave-function. Since then to explore possible topological states has been one of the main driving forces in study of condensed matter physics. The breakthrough took place when Kane and Mele clarified that π electrons on graphene, a honeycomb lattice of carbon atoms open a gap by spin-orbit coupling (SOC) and achieve a topologically nontrivial state called quantum spin Hall effect (QSHE). This discovery has triggered a huge amount of activities in exploring topological states and materials.1)

It is very suggestive to revisit the electronic structure for honeycomb lattice paying attention to the configuration of Berry curvatures. There are two sites in the unit cell of honeycomb lattice. With nearest neighbor hopping, electronic valance and conduction bands touch linearly and thus form Dirac cones at two inequivalent k points, K and K’, locating at the corners of Brillouin zone. It is important to observe that Bloch wave functions exhibit opposite chiral features around K and K’, characterized by opposite Berry curvatures (Fig. 1a). Manipulating the Berry curvatures with physical fields at these two k points can modify the topology of the whole system and realize topologically nontrivial states.

The QSHE is realized by the spin-orbit coupling felt by electrons with additional hopping among next-nearest neighbors (belonging to the same sublattices). The two Berry curvatures for spin-up electrons are positive, while those for spin-down electrons are negative (Fig. 1b). Therefore, QSHE is characterized by zero charge Chern number and nonzero spin Chern number. Another known topological state is the quantum anomalous Hall effect (QAHE), for which all the four Berry curvatures are positive (Fig. 1d), giving nonzero charge Chern number and zero spin Chern number. This state can be realized by staggered flux or circular polarized light.

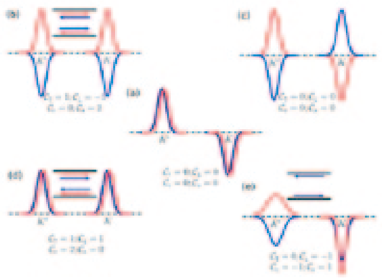

Fig. 1. Possible configurations of Berry curvatures at K and K’ points of honeycomb lattice: (a) CDW, (b) QSHE, (c) SDW, (d) QAHE, and (e) the novel topological state in the present work. Red and blue curves are for spin up and spin down.

2. Research Activities

*(1) Antiferromagnetic Topological Insulator.*2)

We propose a scheme of band engineering by means of staggered electric potential, antiferromagnetic exchange field and the spin-orbit coupling for electrons on honeycomb lattice. With the fine control on the degrees of freedom of spin, sublattice and valley, one can achieve a topological state with three Berry curvatures negative and one Berry curvature positive, characterized by nonzero charge Chern number and nonzero spin Chern number (Fig. 1e). With first principles calculation we confirm that the scheme can be realized by material modification in perovskite G-type antiferromagnetic insulators grown along [111] direction, where Dirac electrons from d orbits are achieved on an atomic sheet of buckled honeycomb lattice. In a finite sample, this state provides a spin-polarized quantum edge current, robust to both nonmagnetic and magnetic defects, with the spin polarization reversible by electric field, and thus is ideal for spintronics applications.

*(2) Nonlocal entanglement via Majorana bound states.*3)

Nonlocal entanglement between two quantum dots (QDs) can be generated through Majorana bound states (MBSs). The two MBSs at the ends of an one-dimensional topological superconductor form a nonlocal electronic level, which couples the occupation states of the two QDs located close to the two ends, and brings the whole system into an entangled state even at low temperatures and zero bias voltage. Upon introducing a charging energy by a capacitor, entanglement of the whole system can manifest itself through the nonlocal entanglement between the two QDs (Fig. 2). The conditional probabilities of electron occupation on one QD with and without electron occupation on the other QD deviate from each other, with the difference proportional to the concurrence of quantum entanglement between the two QDs. Therefore, detecting the difference in conditional probabilities, which is achievable experimentally by established techniques, provides an evidence of the nonlocal nature of the fermionic level constructed by the two end MBSs.

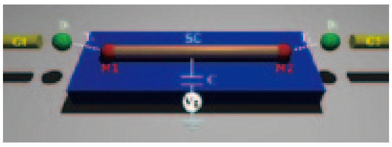

Fig. 2. Schematic setup of 1D topological superconductor coupled with two quantum dots. Charging energy of the superconductor is realized by a capacitor.

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Surface Atomic Scale Logic Gate

MANA Principal Investigator **Christian JOACHIM**
(Satellite at CNRS Toulouse, France)
Toulouse Scientist: Mohamed Hliwa
MANA Research Associate: Maricarmen Grisolia, Romain Julien, Jianshu Jiang, Sandra Garcia-Gil

1. Outline of Research

The Pico-Lab CEMES-CNRS Toulouse MANA satellite is working on the interconnection of a single molecule and DB circuit logic gates and on train of nano-gears, on the design of QHC logic gate. It pursues the exploration of the atomic scale logic gate complexity roadmap to embed the maximum possible computing power inside a single molecule or a surface atomic scale circuit.

2. Research Activities

(1) Atomic scale Interconnects.

Dangling bond atomic wire (DB) are usually LT-UHV-STM constructed by extracting H atoms on Si(100)H or Ge(001)H surfaces. To build up surface atomic scale interconnect to a single molecule logic gate or a DB atomic scale circuit, we have demonstrated that a serious band engineering is required to extract the good atoms at the good position (Fig. 1). The DB wire band gap can be minimized taking into account the surface relaxation[1] and the leakage current due to the background Si bulk doping below the surface.[2] For pseudo ballistic transport, band engineering can now be extended to MoS2 surface DB wires and to surface polymerized molecular wires both studied in MANA-NIMS Tsukuba. Super-tunneling that is tuuneling current with an almost zero decay with length through the wire may be reach by design this way. Atomic scale controlled of a contact between a single starphene and a single Ge(001)H surface DB was obtained to prepare the construction of hybrid molecule-DB circuits.[3]

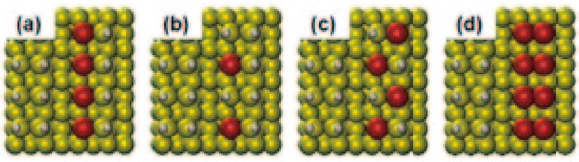

Fig. 1. Four DB wires: (a) single-row, (b) half-row, (c) zig-zag (d) double-row (H in white, Si in yellow and DB in red.

(2) QHC logic gates.

To extend QHC logic gate design from molecules to DB circuits, the role of the symmetry of the calculating block in a QHC Hamiltonian was analyzed. An elegant mathematical demonstration was found showing that it is enough to play with the eigenvalue problem determinant of this matrix to determine the possible QHC logic gates. C3 and C6 symmetries lead to the six 2 inputs known Boolean Logic gate. C2 and C4 are leading only to three of them. This puts a constrain on the design of DB QHC logic as compared to the molecular design of those gates. DB AND and NAND can be designed on Si(100)H. For MANA, the MoS_2 surface may be a better surface combining stability, surface gap and STM DB extraction. For QHC molecules, we have demonstrated that at least 6 inputs are affordable (Fig. 2). This was tested already experimentally with 3 Au atom inputs on a single coronene molecule.[4]

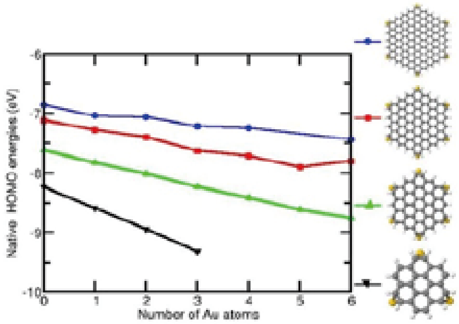

Fig. 2. The linear shift of the ground state of nanographene like molecules as a function of the Au atom inputs with here a maximum of 6 inputs (Coronene is experimental).[4]

(3) Nano-car race.

Mechanical inputs on an atomic scale QHC logic gate are one of our grand objective. We have therefore continued to explore the top down limit of solid state nano-scale gears nanofabrication and nanomanipulation down to 35 nm in diameter, 6 teeth with a 15 nm thickness. One order of magnitude down are required to be able to latch a single molecule switch on a QHC logic gate by such solid state nano-gears with the advantage of a potential input bandwidth orders of magnitude larger than a pure electronic access. To attract attention to single molecule mechanics in general, we have decided to launch a nano-car race.[5] This will have the fantastic advantage to push the technology of the Toulouse MANA satellite LT-UHV 4 STM up to a point that 4 different molecule-cars can be driven independently on the same Au(111) surface for the race. Developing an instrument is very essential also for interconnecting a single QHC logic gates to the external world. This nano-car race has attracted a lot of attention and 6 teams around the world have already registered (Fig. 3).

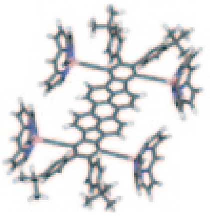

Fig. 3. The Toulouse MANA satellite molecule-car registred for the 2014 first International Nanocar Race.

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Integration of Nano Functionality for Novel Nanosystems

MANA Principal Investigator	**Tomonobu NAKAYAMA**
MANA Scientist	Takashi Uchihashi, Yoshitaka Shingaya, Osamu Kubo, Katsumi Nagaoka
MANA Research Associate	Rhiannon Creasey, Yoshizawa Shunsuke
Visiting Scientist	Seiji Higuchi, Shinichi Machida, Masato Nakaya, Makoto Sawamura, Masami Suganuma, Shin Yaginuma
Graduate Student (Univ. of Tsukuba)	Toshiyuki Kakudate, Amir Pakdel

1. Outline of Research

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

MP-SPM has simultaneously and independently controlled 2 to 4 scanning probes[1,2] which are brought into electrical contact to a single nanostructure and reveals its electrical property.[2,3] The latest development on MP-SPM system is a realization of Kelvin force microscope imaging over the area biased by the probes of multiple-probe atomic force microscope (MP-AFM).[4]

Fabrication of functional nanostructures and nanomaterials is an important part of our research towards a realization of functional nanosystems. For example, surface superconductivity for quantum computing and neuromorphic network architecture for massively parallel analog computing (brain-type computer) are of our interests.

2. Research Activities

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

We realized non-contact potential imaging over a biased nanostructures by means of Kelvin force microscopy (KFM) implemented in our MP-AFM.[4] An example of characterization with the MP-AFM-KFM is presented in Fig. 1. Fig. 1a shows the AFM topography of a grapheme flake on a SiO_2 substrate. The image was constructed from three of four AFM images simultaneously acquired with MP-AFM. Then we could use the probes P3 and P4 in Fig. 1a as electrical terminals to flow current through grapheme and use the probe P1 for KFM measurements over the area under a current field (indicated by small yellow rectangle in Fig. 1a). From the measured KFM image (Fig. 1b), we could measure the potential drops in the graphene flake. This measurement also showed the sheet resistance of this graphene to be about 1.8 kΩ/sq. which was smaller than our previous measurements,[2] suggesting a reduced probability of electron scattering in the area comparable to the length of electron mean free path.

(2) Fabrication of functional nanostructures and nanomaterials.[6-9]

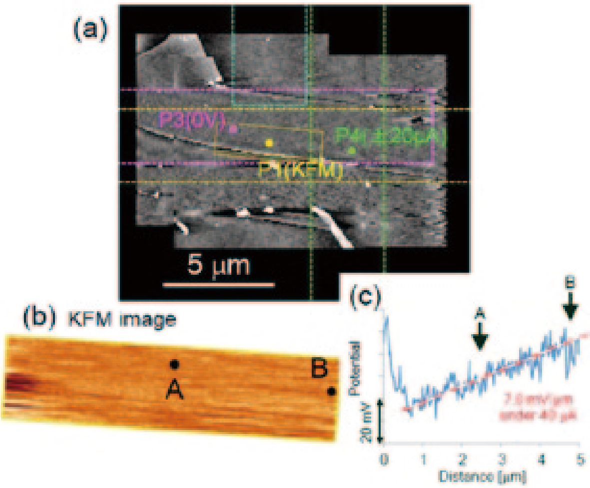

Fig. 1. MP-AFM-KFM measurements of grapheme on SiO_2. (a) Three AFM probes measure the common area and the images are used to determine positional relationships between the probes. (b) While applying appropriate current field between two probes (P3 and P4), the probe P1 measures potential distribution over the area indicated by small yellow rectangle in (a). (c) From the potential map (b), potential drop between A and B shown in (b) can be measured.

We formed a network of carbon nanohorns (CNHs) aggregates which are functionalized by incorporating silver acetate (AgOAc). Investigation with MP-AFM showed that noise in an electrical signal through the CNHs network exhibits 1/f behavior, suggesting a self-organized criticality in the CNHs network as observed in a neural network.[7] For further extending neuromorphic architecture, we developed a peptide molecule which self-assembles into conductive nanofibers.[8] We expect self-organized flexible signal processing with the conductive the peptide nanofibers.

Single-molecule manipulation is still an important and challenging task to attain novel functionalities to controlled molecular nanosystems.[9] For this purpose, a newly designed rotor molecule with reduced symmetry was studied under collaboration with Dr. K. Ariga and Dr. J. Hill of Supramolecules Unit, MANA. Preliminary results showed a possibility of single-molecule level control of molecular rotation on a metal substrate.

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Mesoscopic Superconductivity and Quantum Information Physics

MANA Principal Investigator **Hideaki TAKAYANAGI**
(Satellite at Tokyo Univ. Sci., Japan)
MANA Research Associate S. Kim,
Guest Researcher R. Ishiguro, K. Tsumura
Graduate Student M. Kamio, T. Hayashi, K.Muranaga, M. Yakabe, K. Yokobatake

1. Outline of Research

Our research topic is so-called mesoscopic superconductivity which aims to explore new quantum phenomena in different kind of superconducting devices and to apply them to quantum information physics. We are now developing an ultimate SQUID (Superconducting Quantum Interference Device), i.e., a nano-SQUID which can detect single or several spins. We will also clarify the quantum interaction between a nano-SQUID with embedded quantum dots and spins in dots. This leads to the implementation of an entangled state between a superconducting qubit and spin qubit. The combination of these qubits is a promising candidate for a quantum interface that will be indispensable in the future quantum information network. We are also working on superconductor-based Light Emitting Diode. Superconductor-based LED is expected to be the key device in quantum information technology because of its promising giant oscillator strength due to the large coherence volume of the superconducting pairs together with the possibility of the *on-demand* generation of entangled photon pairs. Our other research targets are (i) transport of self-assembled InAs nanoring and (ii) chiral p-wave hybrid SQUID.

2. Research Activities

(1) Transport of Self-assembled InAs Nanoring.

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

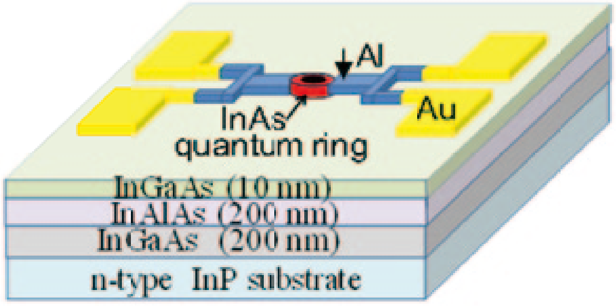

Fig. 1. Schematic view of the sample.

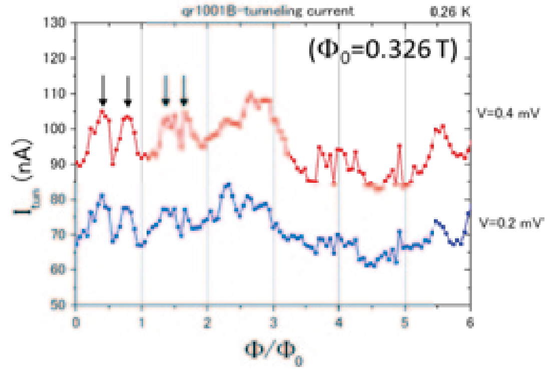

Fig. 2. Tunneling current as a function of magnetic field.

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

We have fabricated a hybrid SQUID with narrow channel of a chiral p-wave superconductor Sr_2RuO_4 and measured interference patterns of magnetic fields and Shapiro steps under micro wave irradiation. Both dc and ac Josephson effect show the existence of h/4e periodicity. The origin of the $h/4e$ periodicity is sin2$\boldsymbol{\theta}$ current of a chiral domain junctions which is different orbital angular moment of the cooper pair. And the existence of sin2$\boldsymbol{\theta}$ term makes clear time reversal symmetry breaking of the supercurrent of Sr_2RuO_4 (Fig. 3).

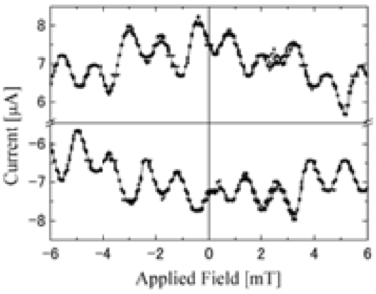

Fig. 3. An evidence of broken time reversal symmetry. There is a clear asymmetry between positive and negative critical currents.

Barrier Inhomogeneities at Vertically Stacked Graphene-Based Heterostructures

MANA Principal Investigator **Kazuhito TSUKAGOSHI**
MANA Researcher Shu Nakaharai
MANA Research Associate Yen-Fu Lin

1. Outline of Research

An integration of graphene and other atomically flat, two-dimensional materials has attracted much interest and been materialized very recently. An in-depth understanding of transport mechanism in such a heterostructure is essential. In this study, vertically stacked graphene-based heterostructure transistors are manufactured to elucidate the mechanism of electron injection at the interface. Temperature dependence of electrical measurements has been carried out over the temperature range of 300 to 90 K. Through the careful analysis of current-voltage characteristics, an unusual decrease of effective Schottky barrier height and increase of ideality factor are observed with decreasing temperature. The model of thermionic emission with a Gaussian distribution of barriers can precisely interpret the conduction mechanism. Furthermore, mapping of effective Schottky barrier height is unmasked as a function of temperature and gate voltage. Our result offers significant perceptions for development of future layer-integration technology based graphene-based heterostructure.1)

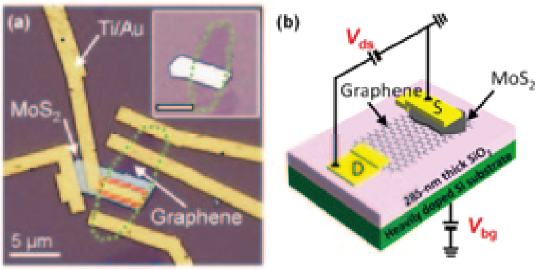

Fig. 1. (a) Optical microscope image of a graphene/MoS_2 heterostructure transistor. The inset shows the heterostructure before the Ti/Au electrodes fabrication process. The scale bar is 5 µm. The dashed line and the solid line depict the frame of graphene flake and effective area of current flow, respectively. (b) Scheme of a graphene-based heterostructure transistor with an overlaid circuit diagram utilized in this study. The heavily doped Si substrate is employed as the back gate. One side of electrode serves as the drain, while the other side is connected to the ground.

2. Research Activities

An optical microscope image (Fig. 1a) and schematic (Fig. 1b) of a graphene/MoS_2 heterostructure transistor with the corresponding image of graphene/MoS_2 heterostructure before the electrode fabrication (inset) are presented. In this structure, I_{ds}-V_{ds} cures of the graphene/MoS_2 transistor at various temperatures were observed (Fig. 2, left). The most pronounced feature is that the I_{ds}-V_{ds} characteristics show a distinctive rectifying behavior at all temperatures measured. The variation between forward and reverse I_{ds} is observed to be in excess of 15 at V_{ds} = ± 0.2 V at RT. According to thermionic emission theory, the I_{ds}-V_{ds} relationship is expressed by

$$I_{ds} = I_0 \exp\left(\frac{qV_{ds}}{nk_BT}\right)\left(1 - \exp\left(\frac{-qV_{ds}}{k_BT}\right)\right) \qquad (1)$$

where q, k_B, and T are the elementary charge, Boltzmann constant, and the absolute temperature in Kelvin, respectively. Based on the thermionic emission, the observed currents were analyzed.

To obtain a better insight into the transport mechanism through the graphene/MoS_2 heterostructure transistors, we adopt the Richardson constant as 54 A/K^2-cm^2 for MoS_2, hence, the effective barrier height and the ideality factor of the graphene/MoS_2 transistor can be derived (Fig. 2, right). The effective Schottky barrier height decreases, while the ideality factor increases with a decrease of temperature. The transport across metal-semiconductor contacts is a thermal assisted process in which electrons solely enable to triumph over a lower Schottky barrier at lower temperatures, resulting in a larger ideality factor. Conversely, as temperature is raised, electron transport is preferably dominated by the current flowing through a higher barrier height.

Here, we estimated possible formation of a spatially inhomogeneity of barrier height. The mean Schottky barrier heights for the graphene/MoS_2 transistors were estimated to be 0.44 eV. The derived value of the standard deviation of Gaussian distribution were larger than 10% contribution of the mean Schottky barrier height in our heterostructure transistor, as a result of the observation of strong temperature dependence of the Schottky barrier height. The effective Schottky barrier height can be further altered by sweeping the gate voltage, leading current modulation. More interestingly, the applied gate volt-age changes the height of Schottky barrier, but does not carve its shape of barrier ridge.

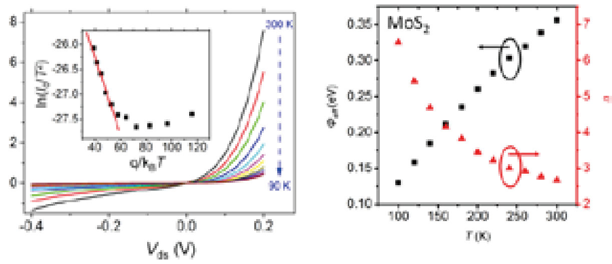

Fig. 2. (Left) I_{ds}-V_{ds} curves of the graphene/MoS2 transistor at various temperatures. The inset shows the corresponding $\ln(I_0/T^2)$ versus q/kBT plot. The solid line in red is a guide to eyes. (Right) Effective barrier height and ideality factor as a function of temperature for the graphene/MoS_2 transistor.

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Nanoarchitectonics of Hybrid Artificial Photosynthetic System

MANA Principal Investigator **Jinhua YE**
(Field Coordinator)
MANA Research Associate L. Liu, Q. Kang, H. Zhou
Graduate Student H. Xu, J. Guo, X. Meng, G. Liu

1. Outline of Research

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

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

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

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

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

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

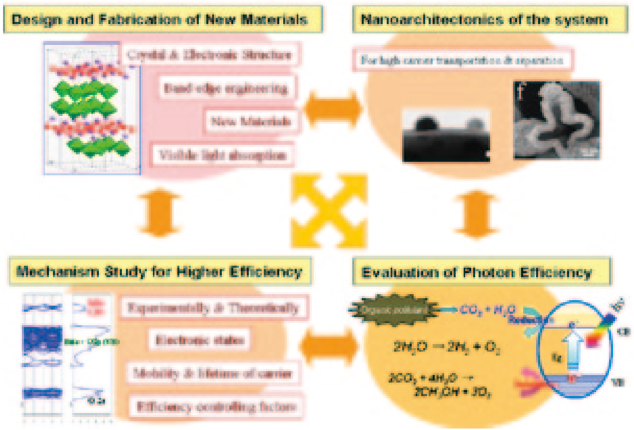

Fig. 1. Four sub-themes and their organic coordination for conducting effective materials exploration research.

2. Research Activities

(1) An effective approach to achieve artificial photosynthetic system: Learn from Nature.[1)]

By using leaves of cherry tree as the template, we have successfully fabricated $SrTiO_3$ photocatalyst with the 3D hierarchical architectures that mimic the structure of leaf's multi-scaled levels (Fig. 2). As a result of efficient mass flow/light harvesting network relying on the morphological replacement of a concept prototype-leaf's 3D architecture into perovskite titanates, the conversion efficiency of CO_2 into hydrocarbon fuels (CO and CH_4) has been significantly improved.

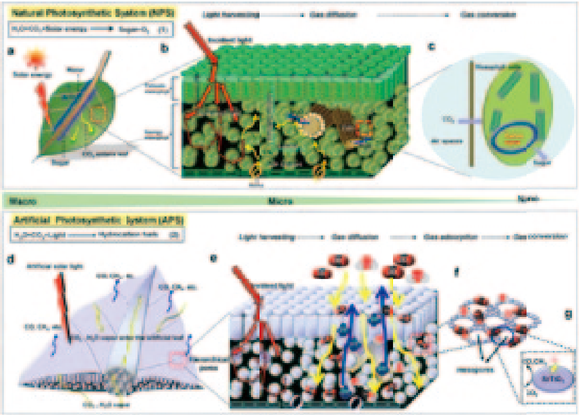

Fig. 2. Schematic illustration and comparison of the key processes in natural photosynthetic system (NPS) and artificial photosynthetic system(APS).[1)]

(2) Realization of visible-infrared light harvesting by Au nanorods "photosensitized" TiO_2 based on LSPR.[2)]

By controlling aspect ratios of Au nanorods, we have successfully turned the localized surface plasmon resonance (LSPR) of Au from 630 nm to 810 nm (Fig. 3). Such an Au NRs "sensitized" TiO_2 can harvest broadband visible even near infrared light, and decompose volatile organic compounds IPA efficiently under visible light irradiation.

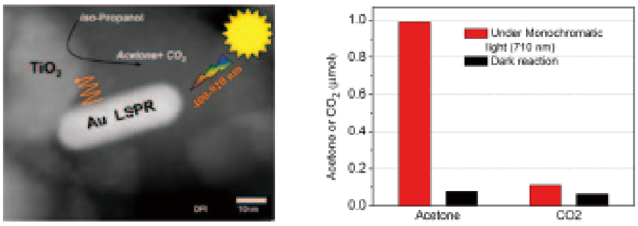

Fig. 3. (Left) Image of photocatalytic reaction by Au NRs "sensitized" TiO_2. (Right) Photocatalytic degradation of IPA under irradiation of monochromatic light (710nm).[2)]

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Solid-State Batteries

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

1. Outline of Research

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

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

2. Research Activities

(1) Orientation control of $LiCoO_2$ epitaxial films.[1)]

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

We have already succeeded in epitaxial growth of single crystal $LiCoO_2$ on sapphire substrates by pulsed laser deposition (PLD). However, $LiCoO_2$ has a layered structure, and thus anisotropies will be found in various electrochemical properties including ionic transport. Therefore, the crystal orientation in the epitaxial films also has to be controlled in order to get to the nature of the interfacial phenomena.

The orientation is controlled by growing the films on different crystal planes of $SrTiO_3$ substrates. For example, a $LiCoO_2$ film grown on $SrTiO_3$ (100) plane is (104)-oriented with its *c*-axis parallel to <111> axes of $SrTiO_3$, as revealed in Fig. 1a. The epitaxial relationship is explainable by similarities in the crystal structure. $SrTiO_3$ has a cubic perovskite structure, while $LiCoO_2$ has a rhombohedral crystal lattice, where oxygen arrangement is very similar. Therefore, the epitaxy has cube-on-cube relationship shown in Fig. 1b, resulting in the four-domain structure, as confirmed by the pole figure measurement. In addition, X-ray pole figures for the films grown on different crystal planes of $SrTiO_3$ substrates exhibit that the orientation is controllable to be (018) and (001) on $SrTiO_3$ (110) and (111), respectively.

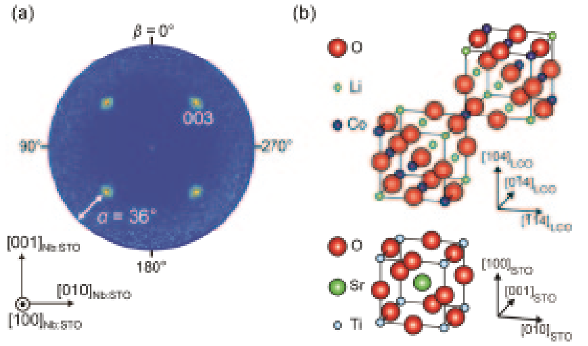

Fig. 1. X-ray pole figure for 003 reflection from a $LiCoO_2$ epitaxial film grown on $SrTiO_3$ (100) substrate (a) and epitaxial relationship between the film and substrate (b).

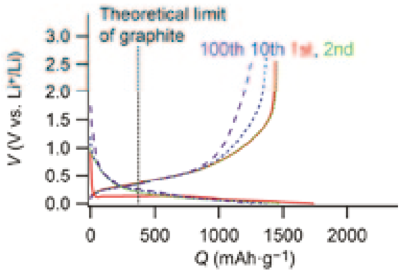

Fig. 2. Charge-discharge curves of a silicon-nitride film prepared by PLD. Thickness of the film is 200 nm, and the charge and discharge rates are 0.1 C and 0.2 C, respectively.

(2) High capacity anode reaction in silicon nitride.[2)]

Insights into the interfacial phenomena will directly lead to high power density and moreover to high energy density indirectly, because high performance interface enables high loading of active materials. On the other hand, a direct approach to achieve high energy density is developing new electrode materials that store large electricity or generate high cell voltage.

Conversion and alloying reactions are known to deliver capacities several times higher than current graphite anodes. This study has revealed that they take place consecutively in silicon nitride; that is, silicon nitride is converted into elemental Si and consecutively the Si is formed into Si–Li alloy with high reversibility.

Fig. 2 shows charge-discharge curves for a silicon nitride, which is fabricated into a thin film by PLD, operated in a solid electrolyte. The silicon-nitride film delivers a high capacity of 1500 $mAh \cdot g^{-1}$, which is four times higher than that of the theoretical limit of graphite anode, in a low potential region. In addition, the silicon nitride shows stable cycling in the solid electrolyte. These results strongly suggest that the silicon nitride is a promising anode material for high-energy solid-state batteries.

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

MANA Principal Investigator **Kohei UOSAKI**

MANA Scientist	Hidenori Noguchi
MANA Research Associate	Bhattacharyya Indrajit, Yuki Morita, Ya Zhang
Graduate Student	Ganessan Elumalai, Cepi Kurniawan, Shuo Yang
Visiting Scientist	Takuya Masuda, Kazuhisa Wada

1. Outline of Research

One of the most challenging problems for chemists/material scientists is construction of efficient conversion systems of energy and materials. In this study, we would like to establish techniques to construct interfacial phases for highly efficient conversion of energy and materials, mainly at solid/liquid interfaces, by arranging metal, semiconductor and organic molecules with atomic/molecular resolution. Furthermore, development of novel methods to characterize the structure and functions of the interfaces in situ and theoretical study are carried out so that structure-function relations should be established and rational design and construction of the desired interfacial phases become possible. Specifically, we have carried out 1. construction of catalytic interfaces by arranging atoms on metal surfaces in ordered manner, 2. construction of photoenergy conversion interfaces by forming ordered molecular layers on metal and semiconductor surfaces, and 3. experimental and theoretical investigations of structure and electron transfer processes at solid/liquid interfaces.

2. Research Activities

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

Development of highly efficient multi-functional electro-catalysts attracted considerable attention because of their important applications for interfacial energy conversion such as fuel cell. Catalytic activities depend on the composition and structure of the catalysts. For example, the atomic ratio giving maximum catalytic activity for electrochemical methanol oxidation reaction, which is one of the most important reactions in fuel cell, is suggested to be $Pt_{50}Ru_{50}$. It is not easy, however, to prepare the catalysts with precise atomic arrangement but we have developed a new method, in which multi-nuclear metal complex is adsorbed on a substrate and then decomposed thermally so that atomically arranged nano-alloys can be formed. Highly dispersed PtRu particles prepared by this technique were demonstrated to show very high electrocatalytic activity and durability for methanol oxidation. This year we have examined the origin of the high activity and durability by XAFS and XPS studies.[1)]

Development of precious metal free electrocatalyst is very important and we have predicted theoretically[2)] and proved experimentally[3)] that BN thin film on Au electrode is an effective ORR catalyst (Fig. 1).

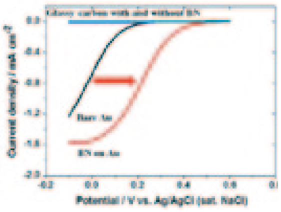

Fig. 1. **Current-potential relations at various electrodes in O_2 saturated H_2SO_4.**

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

It is very important to produce hydrogen from water and form useful compounds by reducing CO_2 using solar energy. Efficiency enhancement of visible light induced up-hill electron transfer at porphyrin-ferrocene thiol modified gold electrode by plasmonic photon-antenna, i.e., gold nanoparticles, was demonstrated,[4)] Pt complexes attached on and within molecular layers formed on Si(111) electrode surface were proved to act as "confined molecular catalysts" for photoelectrochemical hydrogen evolution reaction (HER).[5)]

(3) Experimental and Theoretical 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. We have been using fs visible pump IR probe technique and this year we studied ultrafast charge transfer dynamics of a photoelectrode consisting of CdS nanocluster multilayer assembly.[6)]

Since many techniques used to study solid surfaces in vacuum cannot be used in solution, it is very important to develop new techniques to probe solid/interfaces.

X-ray photoelectron spectroscopy (XPS) is a powerful technique to determine surface compositions, oxidation states and electronic structures of materials of interest but XPS requires vacuum. This year we successfully constructed a novel in situ XPS system, which can be used to study solid/liquid interfaces under electrochemical condition, as schematically illustrated in Fig. 2. A micro-volume cell filled with a liquid is sealed by an ultra-thin Si membrane and is placed in an analysis chamber of XPS. Its operation was demonstrated for potential-induced Si oxide growth in water.[7)]

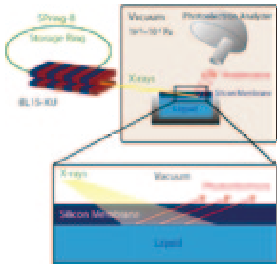

Fig. 2. **Schematic illustration of in situ electrochemical XPS.**

Electrochemical double resonance sum frequency generation spectroscopy (DR-SFG), which uses both tunable IR and visible light and allows simultaneous two-dimensional spectroscopic probe of vibrational and electronic transitions at interfaces (Fig. 3), was developed and applied to reveal the surface electronic state induced by CO adsorption at Pt electrode, which is one of the most important steps of fuel cells with small organic molecules as fuels.

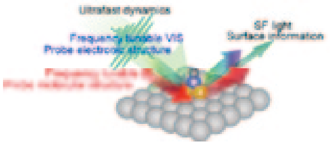

Fig. 3. **DR-SFG to probe interfacial electronic and molecular structures.**

Strong plasmonic coupling of gold nanoparticles with metal substrates, which is used to enhance photoelectrochemical energy conversion efficiency as mentioned above,[4)] is also used to enhance Raman scattering efficiency so that surface molecular structure on well-defined surface can be determined by Raman scattering (Gap mode Raman).[8)]

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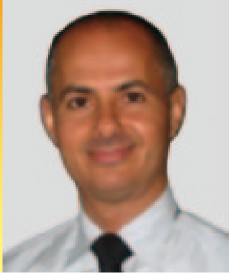
Reticular Materials

MANA Principal Investigator **Omar M. YAGHI**
MANA Scientist Kentaro Tashiro
MANA Research Associate Piramuthu S. Lakshminarayanan, Kappam V. Sajna, Kecai Xiong



1. Outline of Research

The synthesis of mononuclear metal complexes by design is a well-established process. In sharp contrast, however, a protocol for the synthesis of complexes containing multiple homo- or hetero-metals, in a designed fashion, remains largely absent so far, where it is inevitable to get a mixture of products with respect to the number, nuclearity, or sequence of metal centers. In this project so far, we have develop a conceptually new synthetic methodology to create metal complex arrays with controlled number, nuclearity, or sequence of metal centers (Fig. 1).[1–4] This methodology is now opening a new era of metal complex-based materials science by producing multimetallic systems that are inaccessible via traditional synthetic methodologies. Especially, the controlled sequence of metal centers in the arrays, like those in proteins and nucleic acids, will be the most attractive characteristics of this type of materials. Moreover, since our methodology is potentially extendable to automated, parallel processes, high-throughput preparation of the libraries of metal complex arrays will be expected.

2. Research Activities

(1) Enhancement of the Helicity of MOCAs by the Sequence Control of the Metal Centers.[5]

In our studies on the conformations of Metal–Organic Complex Arrays (MOCAs), we found an interesting phenomenon where a heterometallic sequence of the metal centers in MOCA gives rise to the higher helical content in its secondary structure than the corresponding homometallic sequences. When terpyridine (TPy) ligands in a trimer of alanine–alanine–alanine–tyrosine bearing a TPy were fully metallated with Ru(II), Pt(II), or Rh(III), the helical content of the RuRhPt array, as evaluated by its CD intensity at 222 nm, is higher than those of the three homometallic analogues RuRuRu, PtPtPt, and RhRhRh in a wide temperature range (Fig. 1). While further investigations are necessary to see more than the phenomenological things, this observation inspires to think about the meaning of "controlled heterogeneity" in natural science.

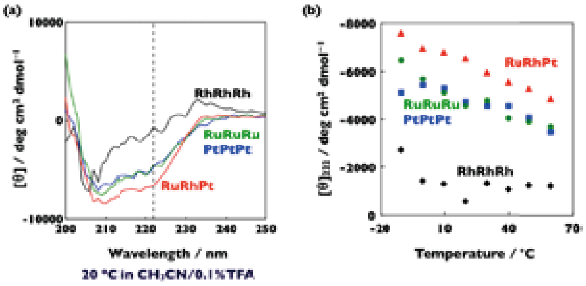


Fig. 1. (a) CD spectra at 20 °C and (b) temperature dependency of their intensity at 222 nm of homo- and heterometallic MOCAs RuRuRu, PtPtPt, RhRhRh, and RuRhPt.

(2) Synthesis of MOCAs with Branched Backbone Structures.[6]

Solid-phase synthesis of MOCAs followed by their successive solution-phase coupling could potentially broaden the variety of accessible molecular network structure of MOCAs. One of the attractive new targets for the application of this improved synthetic approach is MOCA with a branched peptide backbone, which is hard to be prepared by the solid-phase synthesis alone (Fig. 2). With the help of high detectability of newly designed metal complex monomers in MALDI-TOF mass spectrometry, we have successfully demonstrated that MOCAs with triply and quadruply branched backbone structures can be constructed from 4 different metal complex monomers. It is noteworthy that the location of each of 8 metal centers in those MOCA molecules is perfectly controlled in spite of their molecular weights comparable to small proteins as well as necessary reaction steps (> 30) to reach them.

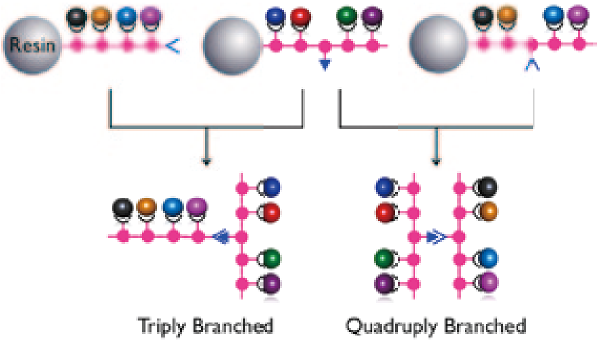


Fig. 2. Synthetic scheme for the construction of MOCAs with branched backbone structures.

(3) Synthesis of TEG-MOCAs.

Due to the currently adopted protocol based on the use of Fmoc-protecting group, MOCAs usually possess this moiety at the *N*-terminal. In order to make MOCAs water-soluble, we replaced hydrophobic Fmoc moiety with hydrophilic TEG moiety. As TEG moiety is also well soluble in a wide range of organic media, targeted MOCAs were purified from simple selective extractions from the crude reaction mixtures into proper solvents such as halogenated carbons and water.

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Dye-Sensitized Solar Cells and Core-Shell Nanowires

Associate Principal Investigator David BOWLER
(Satellite at Univ. College London, UK)

1. Outline of Research

Our ultimate aim is to understand advanced nano-structured materials for applications in photovoltaic devices, as well as future electronic devices. 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. Our research combined experiment and theoretical modeling to give a detailed insight into the properties of the materials. In our new project, we will study the growth and properties of silicon-germanium nanowires to optimize their characteristics, particularly concentrating on the mobility and location of dopants.

We have established a network of collaboration between MANA in NIMS, the Computational Materials Science Center (CMSC) 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 API and the post-doc, as well as visits to UCL from collaborators in NIMS.

2. Research Activities

(1) Atomic and Electronic Structure of Dye Molecules on TiO_2.

Using a recent implementation of delta-SCF DFT in our Conquest code,[1] we have investigated the binding of natural anthocyanidin dyes to the anatase(110) surface, and examined the change in geometry on excitation, as shown in Fig. 1. This builds on previous work on the binding of dyes to amorphous Al_2O_3 layers.[2] We have also studied the effect of Al doping on dye binding and electronic structure on TiO_2,[3] finding that Al can reverse the bad effect of oxygen vacancies in the substrate. We have also investigated the effect of varying the acid binding group to substrates, both in terms of binding strength and resulting electronic structure[4] to optimize the binding motif.

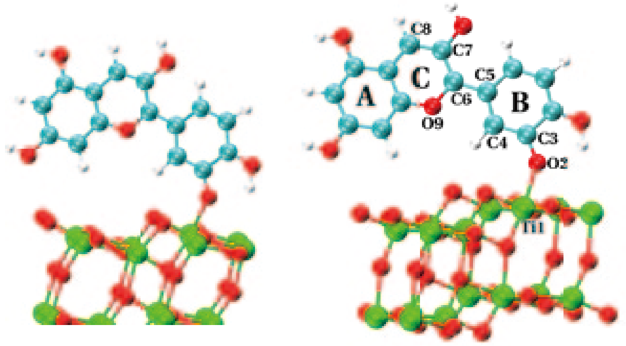

Fig. 1. Binding of cyanidin dye to an anatase TiO_2 surface. Left: Ground state. Right: Excited state.

(2) Dopants on silicon surfaces and in nanowires.

We have recently started 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. We have previously studied dopants such as phosphorus on Si(001)[5] illustrated in Fig. 2, and will build on this existing knowledge to characterise the movement of dopants during growth and annealing, and the effect of dopant location on their electronic properties. We are applying the Conquest code to study these nanowires, in close collaboration with Dr. T. Miyazaki of the CMSC.

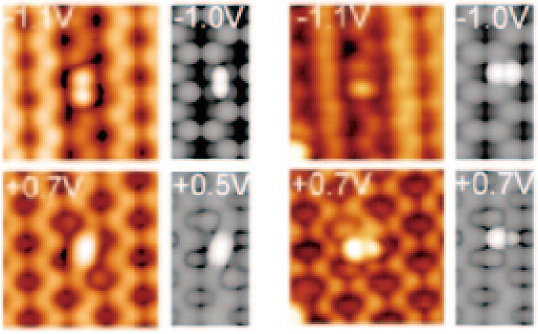

Fig. 2. Comparison of experimental and simulated STM images for P2 molecules on Si(001).

(3) Development of novel methods.

UCL and NIMS have collaborated for many years on the leading linear scaling DFT code, Conquest. This code has been shown to sale to calculations on millions of atoms,[6] and to use up to 25% of the Japanese K computer with near-perfect scaling. We are applying the technique to understanding the structure and function of biomolecules.[7] We are also continuing to develop novel approaches to extend the functionality of Conquest for calculations on innovative materials, concentrating on charge transfer and energetics. We have recently implemented the delta-SCF technique[1] to complement the constrained DFT method already implemented. We are testing a new implementation of time-dependent DFT within the code as a route to reliable energy level calculations for large systems.

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Smart Nano-Biomaterials

MANA Principal Investigator **Takao AOYAGI**
(Field Coordinator)
MANA Scientist Mitsuhiro Ebara
NIMS Junior Young-Jin Kim

1. Outline of Research

The most commonly reported examples of stimuli-responsive materials are poly- (N-isopropylacrylamide)-based one including its copolymers. Stimuli-responsive materials respond to miniscule changes in their environment with drastic changes in their physical properties. In terms of nanomaterials, nanofiber is the most widely used structure because of their biomimetic structure, high specific surface area, high molecular alignment and high porosity compared to films or hydrogels. Recently, we studied the thermal-crosslinkable and temperature-responsive smart nanofiber, which have tunable properties by temperature alternation and demonstrated their potential for cancer therapy.

To achieve this purpose, we have developed a novel self-heating and temperature-responsive nanofiber using magnetic nanoparticles (MNPs) because of their self-heating property by applying alternative magnetic field (AMF). Newly designed the poly(NIPAAm-co-hydroxymethylacrylamide) (abbreviated as poly (NIPAAm -co-HMAAm) in hexafluoroisopropanol and MNPs in distilled water solutions were mixed for electrospinning and the resulting mixture was then subjected to voltage of 20 kV. Thermal crosslinking was carried out at 110°C for 7 h. The fibers preserved their morphology even after thermal crosslinking. Moreover, The MNPs were uniformly dispersed in the nanofibers.

In hyperthermia, the control of generated heat is necessary for reduction of side effects. We checked the time-dependent heating of the nanofiber with different MNP compositions.

2. Research Activities

Hyperthermia, treatment for cancer with elevated temperature in the range of 41-45°C, has been paid attention because it is expected to significantly reduce clinical side effects compared to chemotherapy or radiotherapy and can be effectively used for destroying localized or deeply exist cancer.[1] Since adequate heating of the whole tumor volume is difficult, hyperthermia has been utilized in combination with chemotherapy to increase cellular sensitivity to anticancer drugs. To test both hyperthermia and DOX effects of the DOX/MNP-nanofiber in vitro, the cytotoxicity to human melanoma cell line COLO 679 cells were evaluated by MTT assay for 1, 3, 4 and 5 days (Fig. 1). The cells were cultured at 37 °C for 2 days. MNP-nanofiber or DOX/MNP-nanofiber was then added to the medium and cells were co-incubated at 37 °C for another 24 h. On testing the hyperthermia effect on the cells, an AMF was then turned 'on' at day 3. After 8 min, the temperature of the medium was increased to 45 ± 1 °C and then maintained for up to 5 min. This treatment was repeated again at day 4. The cell viability decreased about 20% in the presence of MNP-nanofiber without DOX in a magnetic field for 5 min duration. Although the cancer cell killing effect was still low, the magnetic field successfully affects cell viability over a period of 5 min. This can be improved as the time of the hyperthermia treatment is increased. In case of the DOX/MNP-nanofiber, on the other hand, cell viability decreased to 70% by AMF application. Although the hyperthermia effect itself showed a minor anticancer effect for a short duration AMF application, DOX released from the nanofibers induced the apoptosis of cancer cells due to a synergistic effect in combination with hyperthermia. Since hyperthermia can kill cancer cells by a number of pathways,[2] including apoptosis, the viability of the cells was also demonstrated by fluorescent staining with annexin V Cy-3 and terminal deoxynucleotidyl transferase-mediated dUTP nick end labelling (TUNEL) assay. In general, apoptosis initially induces the inversion of phosphatidylserin, which allows binding to annexin V. Therefore, annexin V detects an early stage apoptosis while TUNEL assay detect the late stage apoptosis. For MNP-nanofiber, only annexin V stained cells were detected, indicating that the cause of cell death is primarily membrane rapture. For DOX/MNP-nanofiber and free DOX, although TUNEL stained cells were not observed at day 4, both annexin V and TUNEL stained cells were observed at day 5, indicating late-stage apoptosis. These results indicate that the double effect of DOX treatment and hyperthermia effectively induced apoptosis while the effect of a single hyperthermia on apoptosis was not significant for a short time AMF treatment.

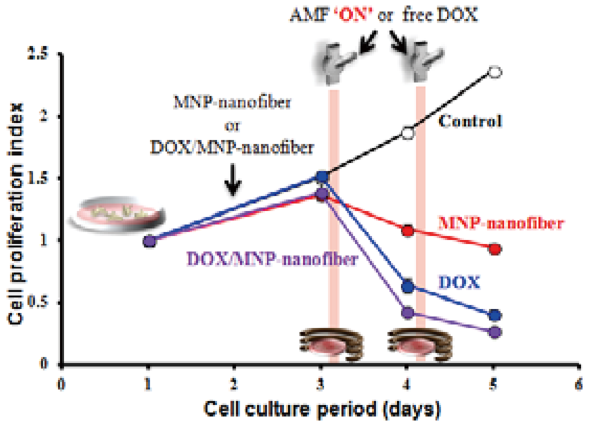

Fig. 1. In vitro anticancer tests involving the DOX/MNP-nanofibers and human melanoma (COLO 679) cells.

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Long-Term Stem Cell Labeling by Collagen-Functionalized Single-Walled Carbon Nanotubes

MANA Principal Investigator **Guoping CHEN**
MANA Scientist Naoki Kawazoe
MANA Research Associate Ida Dulinska-Molak
NIMS Junior Researcher Hongli Mao

1. Outline of Research

A critical aspect of stem cell-based therapies is to distinguish the implanted cells from the host cells and to monitor them in terms of their viability, migration, distribution and the relative contribution from the delivered cells versus host cells. With this respect, a long-term and non-invasive *ex vivo* labeling method for stem cells is critically needed. Genetically encoded luciferase and fluorescent proteins such as green fluorescent protein are commonly used for stem cell labeling and tracking. However, these methods require complicated genetic modification of the stem cells and are hard to avoid the overlap with the autofluorescence signals. On the other hand, carbon nanotubes (CNTs), especially single-walled carbon nanotubes (SWCNTs) have been extensively explored for biological and medical applications motivated by a consequence of their unique physical and chemical properties. One of the most attractive advantages of SWCNTs is that they can penetrate the biological barriers and be internalized by cells effectively in an energy dependent or independent manner.

In this study, collagen-functionalized SWCNTs (Col-SWCNTs) were used as a probe to label and image human mesenchymal stem cells (hMSCs). Internalization of Col-SWCNTs into hMSCs was conformed. The viability and differentiation capacity of the labeled hMSCs were investigated via WST-1 assay and osteogenic and adipogenic differentiation-induction experiments, respectively. The cells could be detected by Raman microscope easily even after 2 weeks of culture post labeling, revealing the Col-SWCNTs should be an useful probe for long-term stem cells labeling.1)

2. Research Activities

The SWCNTs used for stem cells labeling were firstly coated with collagen to improve their dispersibility in water. The Col-SWCNTs retained the inherent properties of SWCNTs and the aqueous suspension was stable for months.2) Most of the Col-SWCNTs were individually dispersed in the aqueous suspension. TEM obeservation revealed the lattice spacing of individual carbon layer and surface of the nanotube was coated by collagen. A key premise for ectogenous agents based cell labeling is that the agents can be efficiently internalized by the cells. To label hMSCs, P4 cells at a density of 5,000 cells/cm^2 were cultured with DMEM containing Col-SWCNTs at a concentration of 5 μg/mL for 48 hours. The labeled cells showed black color due to the color of the carbon nanotubes. The average amount of internalized SWCNTs in each cell was 2.17 ± 0.34 pg. In other words, the average number of internalized SWCNTs in each cell was $7.68 \pm 1.20 \times 10^6$. A high amount of Col-SWCNTs were internalized by cells, which should suffice to label and image the hMSCs efficiently. The internalized Col-SWCNTs were further confirmed by confocal Raman imaging. The morphology of hMSC including the cell shape, nucleus position and cell extension was revealed through the phase-contrast image and the measured plane was focused on the nucleus of the cell. The labeled hMSC showed strong Raman signals around the nucleus, suggesting the internalized Col-SWCNTs were primarily located around the nucleus. Absence of the indicative G-band Raman peak of SWCNTs at 1590 cm^{-1} in Raman spectrum I which was obtained from the position out the cell (no cell region) revealed no SWCNTs were detected at the outside of cells.

Live/dead double staining showed that few dead cells were detected, suggesting that most of the cells were viable no matter being labeled with Col-SWCNTs or not. The results of WST-1 assays on the metabolic activity (cell viability) of the Col-SWCNTs labeled hMSCs showed no obvious difference was observed between the experimental and the control groups, indicating that Col-SWCNTs exhibited no obvious cytotoxicity on hMSCs. Otseogenic and adipogenic differentiation experiments showed that labeling with Col-SWCNTs did not affect the differentiation capacity of hMSCs. Although incorporation of Col-SWCNTs did not affect cell viability and differentiation, the Young's modulus of MSCs increased after SWCNTs incorporation.3)

Another problem in stem cell labeling and imaging is that the ectogenous labeling agents may be released from the labeled cells and internalized by other nearby cells, which can cause a false-positive result. It has been reported that CNTs can be expelled from cells through exocytosis after internalization over hours or days. However, in our previous study, we found that Col-SWCNTs were retained in bovine articular chondrocytes for over a week and the prolonged dwell time of Col-SWCNTs in cells should be attributed to the bioactive collagen on the surface of nanotubes.1) To conform whether the Col-SWCNTs were released from the labeled hMSCs and internalized by the nearby unlabeled hMSCs, an inverse co-culture system was used to co-culture the unlabeled hMSCs and the Col-SWCNTs labeled hMSCs. The results indictaed that almost all of the internalized Col-SWCNTs could dwell in hMSCs for a long period of time. These results suggest the potential of collagen functionalized SWCNTs as a probe for long-term stem cell labelling and imaging.

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Nanotherapeutics Based on Redox Polymer Nanoarchitectonics

MANA Principal Investigator **Yukio NAGASAKI**
(Satellite at Univ. Tsukuba, Japan)
Lecturer Yutaka Ikeda
Post-doc Yukichi Horiguchi, Toru Yoshitomi

1. Outline of Research

The objective of our research is to create new bioactive materials for high performance therapeutic system. In order to use materials in vivo, interactions between materials surface and bio-components such as blood and tissue must be controlled. Non-biofouling surface is one of the most important characters for design of high performance biomaterials. Using our surface constructing technique thus developed, we have developed novel bionanoparticles. Highly dispersion stable and biocompatible nanoparticle is known to increase its blood circulation tendency. In order to control these nanoparticles in vivo, we have to install further specific functionality via new concept by novel materials nanoarchitechtonics technique. In 2013, we have developed novel redox polymers as new biomaterials. One of our new materials, which can be utilized as a matrix for oral drug delivery system and also peritoneal dialysis.

2. Research Activities

(1) Preparation of silica-containing redox nanoparticles (siRNP) and application for peritoneal dialysis.

Recently, technological developments in renal replacement therapy (RRT) have been used to successfully treat patients with renal failure. By the end of 2010, 2.03 million patients were undergoing RRT. Nearly 90% of these patients received hemodialysis (HD) therapy, while worldwide only 8.4–11% were treated with peritoneal dialysis (PD). Although HD substitutes for a portion of renal function, there still remains several issues such as: 1) The continuous need for hospital attendance, which limit the social activities of patients; 2) insufficient removal of medium molecular weight uremic toxins; and 3) the removal of body fluid in a short time thereby leading to cardiac overload and vascular damage. These issues increase in terms of patient risk for several serious diseases such as stroke and myocardial infarction. In contrast, the following reasons make PD the first choice of RRT in many countries: 1) Low load in terms of medical economies; 2) social precedence during domiciliary treatment; and 3) medical advantages with respect to patient outcome. For the last reason in particular, current studies are successively revealing the advantages of PD-first policy as they relate to residual renal function and survival rates. For example, dialysate can be changed by oneself. In addition, rehabilitation is easy, it maintains renal function, and the risk of stroke and myocardial dysfunction is low. Thus, PD has much potential to provide high quality of life to patients who are undergoing RRT.

However, the long-term outcome of PD is still poorer than that of HD. Two major reasons for this are: 1) The insufficiency of dialysis due loss of peritoneal function, which thus increases changes in dialysate; and 2) the occurrence of encapsulating peritoneal sclerosis (EPS), which is a fatal complication of PD. Chronic inflammation of peritoneal membrane leads to encapsulation of the intestine, which then results in severe ileus and malnutrition in EPS patients. Dialysate with a high glucose concentration causes oxidative stress to the peritoneum and results in EPS over the course of several years. Frequent changes in dialysate increase the risk of contracting infectious diseases. Resolving these would not only increase the quality of life for the patient, but also reduce medical costs worldwide. For these objectives to be met, both a decrease in oxidative stress to the peritoneal membrane and an increase in the adsorption capacity of blood wastes are required.

We have previously developed novel nanotherapeutics with redox nanoparticles (RNPs) containing nitroxide radicals as free radical scavengers for treating cerebral and renal ischemia-reperfusion, as well as brain hemorrhage. Typical characteristics of RNPs are: 1) Because nitroxide radicals are covalently conjugated to the nanoparticle backbone, they are not leaked to the outside of the nanoparticle; 2) the sizes of RNPs are ca. 40 nm in diameter and thus they are not internalized into healthy cells; and iii) as a consequence RNPs do not interfere with normal redox reactions inside of cell. These characteristics help RNPs selectively scavenge over-produced reactive oxygen species (ROS), especially outside of the cell. We have so far confirmed the therapeutic effects of RNPs with respect to several disease models such as cerebral and renal ischemia reperfusion injuries, cerebral hemorrhage, cancer, ulcerative colitis, and small intestinal inflammation.

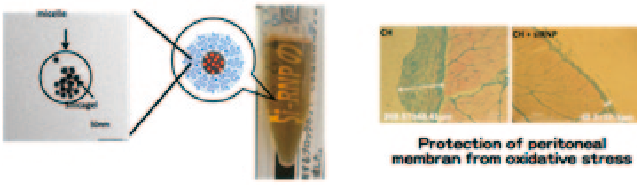

Fig. 1. Design of Silica-containing Redox Nanoparticle for peritoneal dialysis.

The objective of this study was to apply RNPs as one of the components in dialysate to reduce oxidative stress. Porous silica nanoparticles were combined with RNPs in order to enhance the adsorption capacity of creatinine and other LMW compounds effectively (Fig. 1). The silica-containing RNPs (siRNPs) thus prepared were confirmed to increase the adsorption capacity of uremic toxins in vivo. EPS model rats were prepared by injecting them daily with chlorhexidine gluconate (CH) intraperitoneally (i.p.) for a week. siRNPs was administered to the peritoneal cavity of the rats at the same time to confirm that they were protected against CH-induced inflammation. CH-induced dysfunction of peritonitis such as disruption of the mesothelial cell layer and vascularity of the expanded submesothelial compact zone was not observed for the siRNPs treatments. These results show potential for siRNPs to be used as a new multi-functional nanomaterial in peritoneal dialysis.

Nanoarchitectonics-Driven Interfaces and Nanoparticles for Therapeutic Applications

MANA Principal Investigator **Françoise M. WINNIK**
(Satellite at Univ. Montreal, Canada)
Post-doc C. Agudelo, J. Niskanen (Univ. Montreal);
Y.T. Richard Lau (MANA)
MANA Scientist P. Kujawa

1. Outline of Research

Materials Nanoarchitectonics has led to important innovations in the design and construction of systems in nanoelectronics, nanomachinery, and energy conversion. Our research aims to use this approach to address current challenges in nanomedicine, placing emphasis on agents for therapeutic and diagnostic applications.[1,2] Specifically, we have employed the five technologies of Materials Nanoarchitectonics (Fig. 1) (i) to engineer interfaces able to control cell aggregation and gain insight into tumor genesis; (ii) to modify boron nitride nanotubes for uses in theragnostics, and (iii) to design new delivery agents against inflammation.

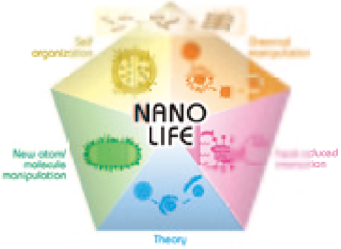

Fig. 1. Five pillars of Materials Nanoarchitectonics for theragnostics applications (reprinted from ref. 1, copyright 2013 ACS).

2. Research Activities

(1) Regulation of cell aggregation on nanoengineered polysaccharide interfaces.

We discovered that chitosan-phosphorylcholine (CH-PC) coatings[3] can be used to induce cellular aggregation analogous to the formation of tumors. Moreover, the level of cellular aggregation is adjustable by dialing-in the amount of PC groups incorporated in chitosan (Fig. 2). In parallel, the CH-PC films were characterized by surface plasmon resonance and quartz crystal microbalance with dissipation. These studies indicate (i) that the bulk mechanical properties of the films (elasticity) are not affected by the level of PC group incorporation and (ii) that the PC groups migrate towards the surface of the films, where they participate in a concentration-dependent way to the film/protein interactions and to cell aggregation.

The films present promising characteristics for fundamental studies of cancer development and for the evaluation of the efficiency of anticancer drugs against tumor growth in surroundings more relevant to real life situations than single cell studies.

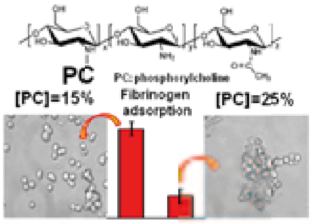

Fig. 2. CH-PC films with adjustable level of film/ protein interaction and cellular aggregation (shown here for MCF-7 breast cancer cells).

(2) Surface engineered boron nitride nanotubes (BNNT) for theragnostics applications.

In collaboration with the group of D. Goldberg, we designed an efficient method to coat pristine BNNTs with a uniform nano-sheath made of biopolymers. This entirely new process[4] (Fig. 3) offers a rapid, mild, and scalable route for de-bundling BNNTs and converting them in a single process into water-dispersible biofunctional BNNTs that may serve as drug delivery vehicles or scaffolds in tissue engineering. By this method we obtained intact BNNTs uniformly coated throughout their length with a 10–20 nm thick sheath of either cationic, anionic or zwitterionic polysaccharides, such as chitosan, hyaluronic acid and chitosan-PC. Of note, the process conception was driven by theoretical calculations and used self organization and field-induced interactions, three tools of Materials Nanoarchitectonics. Current studies include the evaluation of the cytotoxicity of polysaccharide-coated BNNTs and of their mode of internalization into cells.

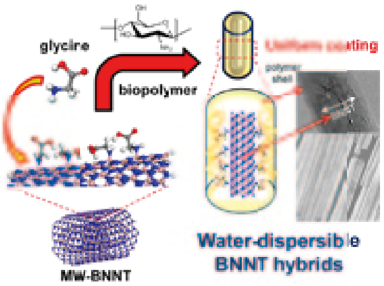

Fig. 3. Coating of boron nitride nanotubes with biopolymer leading to water-dispersible biofunctional BNNTs.

(3) Polymersomes as carriers of active molecules in the treatment of inflammation.

Curcumin, a polyphenol derived from turmeric, is an efficient anti-inflammatory compound. However, it has not been approved as a drug, mostly due to poor absorption and rapid metabolism. To overcome these drawbacks, we encapsulated curcurmin in the membrane of polymersomes formed by an A-B-A triblock copolymer, where A is hydrophilic [poly(2-methyl-2-oxazoline] and B is hydrophobic [poly(dimethylsiloxane)]. Polymersomes loaded with both curcurmin and a peptide are evaluated *in-vitro* and *in-vivo* in studies of inflammatory diseases. This work is carried out in collaboration with Prof. D. Maysinger, McGill University (Montreal, Canada).

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Next-Generation Semiconductor Nanodevices

Group Leader **Naoki FUKATA**
(Nano-Materials Field)

1. Outline of Research

Nanoscale silicon devices using silicon nanowires (SiNWs) such as metal-oxide semiconductor field-effect transistors (MOSFETs) require properties that allow their electrical conductivity to be controlled. Considerable efforts have been directed for developing nanoscale silicon devices. Impurity doping of SiNWs or germanium nanowires (GeNWs)[1-3] is generally performed *in situ* during vapor-liquid-solid (VLS) growth, which has the advantage of not inducing defects. However, there are also certain disadvantages, such as surface doping and tapering structures created by sidewall growth, resulting in non-uniform doping along the growth direction of NWs. Impurity doping is necessary to form source and drain regions in NWs-MOSFETs, while the retardation of carrier mobility due to impurity scattering has to be taken into account when doping the channel region. CoreshellNWs using Si and Ge show potential for suppression of impurity scattering.

In this study, doped impurities and carriers are separated in the core and shell regions, respectively, due to the band offset between Si and Ge, resulting in a markedly low scattering rate between them and improved mobility of free carriers.[4] The concept is shown in Fig. 1.

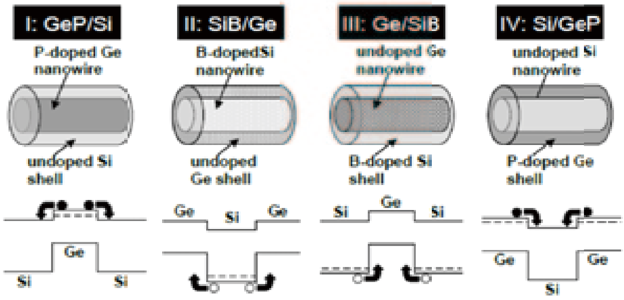

Fig. 1. Schematic illustration of Si/Ge and Ge/Si core-shell nanowires.

2. Research Activities

(1) Formation of Si/Ge and Ge/Si core-shell nanowires.

Four different types of Si/Ge (i-Si/n-Ge, p-Si/i-Ge) and Ge/Si (n-Ge/i-Si, i-Ge/p-Si) core-hell NWs were prepared by CVD to realize the band structures illustrated in the insets of Fig. 2. To confirm the formation of Si/Ge and Ge/Si core-shell NWs, EDX measurements were first performed during TEM measurements. The results obtained for a shell growth time of 30 s are shown in Fig. 2a-d. The red represents Si and blue represents Ge. These results clearly show the formation of Si/Ge and Ge/Si coreshell NWs. We also carefully checked the crystallinity of the shell in Si/Ge and Ge/Si core shell NWs and observed clear lattice fringes in the shell regions (Fig. 2e-g).

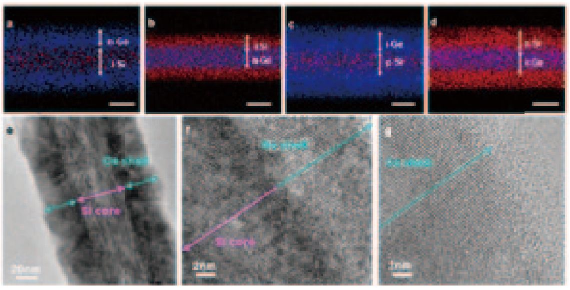

Fig. 2. EDX images of (a) i-Si/n-Ge, (b) n-Ge/i-Si, (c) p-Si/i-Ge, and (d) i-Ge/p-Si core-shell NWs. The scale bar represents 20 nm. The red represents Si and blue represents Ge. TEM images of i-Si/n-Ge are shown in (e), (f) and (g).

(2) Site selective doping in core-shell nanowires.

To confirm P and B doping in the four different types of Si/Ge and Ge/Si NWs, we performed the Raman measurements shown in Fig. 3. The local vibrational peaks of P and B atoms and Fano broadening in the optical phonon peaks were observed using Raman scattering methods. The Fano interference shows the electrical activity of dopant atoms.These results demonstrated that the B and P atoms are selectively doped into the shell and core regions and electrically activated in the substitutional sites, showing the success of site-selective doping.

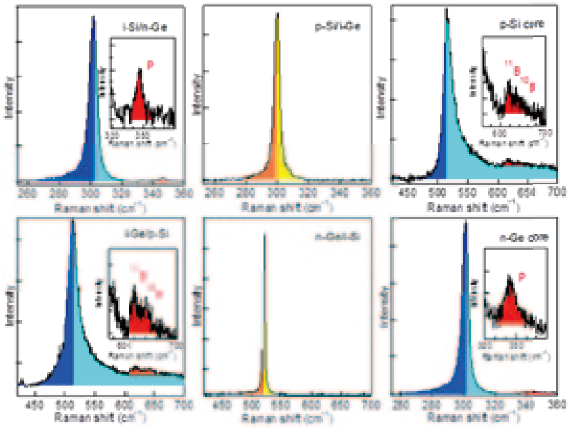

Fig. 3. Raman spectra observed for (a) i-Si/n-Ge, (c) p-Si/i-Ge, (f) i-Ge/p-Si, and (h) n-Ge/i-Si core-shell NWs. Raman spectra observed for (d) p-Si core NWs and (i) n-Ge core NWs. Insets (b) and (j) are the magnification of the P local vibrational mode in the n-Ge shell layer and the n-Ge core, respectively. Insets (g) and (e) are the magnification of the ^{11}B and ^{10}B local vibrational peaks in the p-Si shell layer and the p-Si core, respectively.

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Development of Nano Biomedicines

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

1. Outline of Research

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

2. Research Activities

(1) Immunosuppressive DNA nanomedicine against autoimmune disorders.

Innate immune responses represent the first line of defense against pathogens such as bacteria, virus, fungi and parasites. First step to induce innate immunity is the recognition of pathogens by “pattern recognition receptors (PRR)”. Cytosolic DNA sensor proteins such as DAI, IFI16 and RNA polymerase III, which are PRR, sense pathogen’s DNA followed by a signaling cascade in the cells that leads to the production of immune-mediator cytokines such as interleukin-6 (IL-6) and interferon-β (IFN- β). However, recently it is reported that the DNA sensor proteins also sense own DNA from dying cells, leading to the production of these cytokines, which results in autoimmune disorder. The purpose of this study is to find a way for suppression of cytokines induced by an interaction of self-DNA with DNA sensor proteins.

The strategy is to suppress these immune-mediator cytokines using synthetic oligodeoxynucleotides (ODN) that has a higher affinity to DNA sensor protein than B-DNA. To find ODN that has a potential to suppress the cytokine induced by B-DNA, three ODNs with different base sequences (CpG ODN, GpC ODN and CpG free ODN) were examined the suppression effect of these ODNs. Consequently, we observed slight suppression effect on both IL-6 and IFN-β in naked single-strand (ss) CpG ODN that contains cytosine-guanine (CG) dinucleotide sequence. This suppression effect was greatly enhanced by CpG ODN complexed with cationic lipid but not cationic silica nanoparticles. In addition, ds CpG ODN complexed with cationic lipid had more suppression effect. This study demonstrates that ds CpG ODN complexed with cationic lipid can be applied for the treatment of autoimmune disorders.

(2) Development of intracellular delivery system for DNA drugs.[1,2]

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

(3) Safety and toxicity assessment on nanomaterials.[3,4]

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

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Bioactive Ceramics Materials

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

1. Outline of Research

Bioactive ceramics is divided into two types. One is conventional one that can directly bond with bone but not influences cell functions so much. Another type can activate target cell functions. We have been investigating both type of bioactive ceramics and ceramic/polymer composites for tissue regeneration. In recent years, we have been investigating the NIMS original material of hydroxyapatite/collagen bone-like nanocomposite (HAp/Col) with high performance in activation of cellular functions and incorporation into bone remodeling process. In fact, the results of clinical tests of the HAp/Col porous body were reported by medical doctors and revealed excellent bone repairing ability at 20.6% higher than conventional bioresorbable ceramics in average. further, 75% of high efficacy ratio was reported for the HAp/Col porous body when repairing large bone defects in which 10-30 ml of materials needed to fill, instead of 0% of that for conventional ceramics.[1)] This material is now commercially available in Japan as "Refit®." We are continuing our investigation for further improvement of its functionalities to utilize it in many medical and dental fields, such as an injectable material, highly bioactive coating on metallic implants, osteochondral scaffold and safer gene transfer. In addition, to support practical use (commercialization) of new biomaterials, studies on bioactive ceramics evaluation methods for establishment of new international standards.

2. Research Activities

(1) Injectable HAp/Col materials.[2)]

Injectable artificial bone with bioresorbability is strongly desired in practical medicine to realize good minimum invasive surgery to reduce potential risk of bone fractures as well as inhibition of new bone formation due to remaining of cements in body. Injectable HAp/Col could be good candidate because of its nature to reduce these risks. We utilize sodium alginate (Na-Alg) for gelation and lubrication agent for injectable HAp/Col. This year we continued to investigate effect of additive in viscosity and anti-decay property. An organic acid or caclcium compound solely used as an additive, we did not show sufficient properties for self-setting injectable bone-filler. In a combination use of them, gelation effect of alginate by acidic pH induced by addition of an organic acid was dominant and not effective to control calcium release ratio. Thus, we are now focusing on calcium compound with appropriate solubility. Preliminary result showed injectable self-setting HAp/Col was prepared successfully. We will show the results in detail in the next progress report.

In addition, we already have prepared scaffold with three-dimensionally controlled microstructure using injectable HAp/Col-Alg without additives by collaborating with Dr. Hui-Suk Yun in KIMS (Fig. 1).

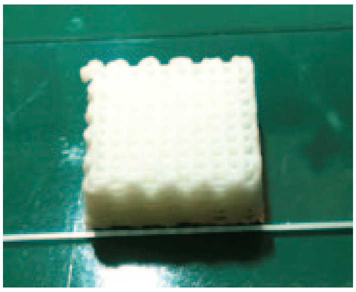

Fig. 1. Hydroxyapatite/collagen self-organized nanocomposite with three-dimensionally controlled microstructure.

(2) Highly bioactive coating on onplant device.[3)]

Hydroxyapatite (HAp) is widely used as a coating materials on metallic implant in medical and dental fields to improve osteoconductivity. This high osteoconductivity introduces early and strong osseointegrated bonding between titanium alloy and bone in artificial tooth roots. For orthodontics, onplant that inserted in between bone and periosteum is commercially available for minimum invasive anchorage device. On the onplant, to accelerate osteoconduction for strong fixation for anchorage, HAp is coated; however, it takes 3-4 months until obtaining sufficient bonding strength for anchorage due to low bone formation ability at subperiosteum site. This year, we tried dip-coating of HAp/Col on titanium wire and compared bone formation ability of HAp/Col-coating at subperiosteum site with that of HAp-coating and bare titanium wires. The results showed that the HAp/Col coated titanium wire showed complete direct bone bonding only after 4 weeks implantation, even HAp-coated titanium wire showed no or very few direct bone bonding as the same as bare titanium wire (Fig. 2). Bone coverage ratio, bone formation height and bonding strength were also the best in the HAp/Col-coating.

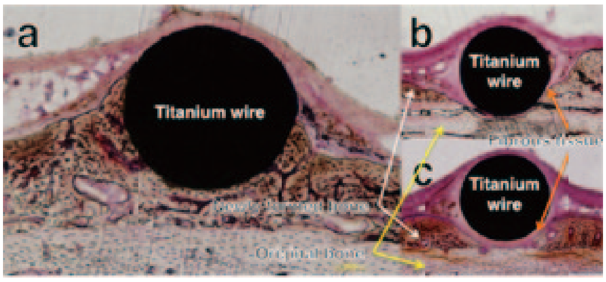

Fig. 2. Titanium wire and surrounding tissues implanted into subperiosteum site for 4 weeks; a) HAp/Col coated, b) HAp coated and c) uncoated.

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Materials for Functional Nanomedicine

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

1. Outline of Research

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

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

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

2. Research Activities

(1) *Vascular-inducing Poly(Glycolic acid)-Collagen Nanocomposite-Fiber Scaffold.*[1,2)]

For regenerative medicine with scaffolds, the immediate cellularization of the scaffold accompanied by angiogenesis inside is an important event. Such the aim is generally pursued by combining basic fibroblast growth factor (b-FGF) or vascular endothelial growth factor (VEGF) with the scaffold. In this study, we produced the nanocomposite nanofiber composed of poly(glycolic acid), PGA, and collagen to accomplish the recruitment of host cells and peripheral blood vessels without the bio-derived matter like growth factors. Structural analysis revealed that the fiber has the sheath-core like structure (Fig. 1) in which the surface region is abundant in PGA and the core region is abundant in collagen. This peculiar fibrous structure probably contributes the fragility of the fiber under the swelling in body fluid. The results of the animal experiment demonstrated that the PGA-collagen nanofiber sponge was entirely populated and vascularized within 5 days after the implantation. We hypothesized that the early fragmentation of the implanted fibrous sponge accelerated the host's inflammation reaction by phagocytized by macrophage, which followed by the recruitment of the fibroblasts and endothelial cells from the host tissue. Designing the suitable nanoscale structure of materials makes cellularization and vascularization of the scaffold possible without bio-derived factors (Fig. 2).

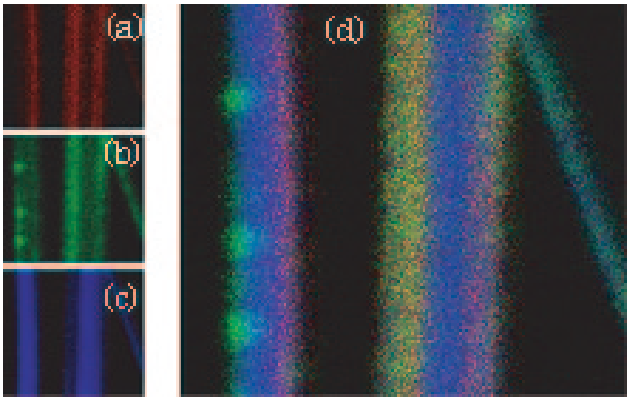

Fig. 1. TOF-SIMS images of the electrospun microfibers of the PGA-collagen. (a) $C_2H_2O_2^+$ which is a decomposition product of PGA. (b) $C_4H_9^+$ which is a decomposition product of PGA. (c) $C_4H_8N^+$ which is a decomposition product of collagen. (d) the merged image of (a)–(c).

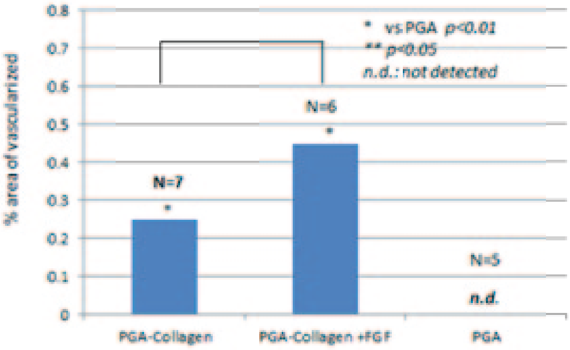

Fig. 2. Comparison of neovascularization effects by different sponge nanofibers. PGA-Collagen, PGA-Collagen +FGF (2.5 microgram), and PGA sponges without FGF were employed. After one week implantation, cross section images were observed from the histological section. And the ratios of area, which calculated from the vascular invaded area against the total area of the sample, were evaluated by using Angiogenesis Image Analyzer software (Kurabo, Osaka, Japan).

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Functionalization of Atomic Network Materials

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

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. The direct conversion of waste heat to electricity is a large incentive to find viable thermoelectric (TE) materials.1) Traditionally, high performance TE materials have tended to not be element friendly; being composed of Bi, Te, Pb, etc. One need exists to develop effective TE materials composed of abundant and safe elements. Another need exists for materials to have good thermal stability when considering mid to high temperature applications. To this end, we aim to functionalize covalent materials composed of elements like XIII~XV group elements (C, B, Si, Al, Sn, etc.) by utilizing their atomic network structure, i.e. clusters, 2D atomic nets, cage-like structures in which the structural order plays a large role in physical properties.2-4)

2. Research Activities

(1) Control of TE properties by atomic network control.

A series of homologous RE-B-C(N) compounds was previously discovered to be the long awaited n-type counterpart to boron carbide.2-4) Compatible materials were further realised.5-7) Finding good p, n matching materials has been one of the large obstacles for TE application. Furthermore, through particular synthesis processes, we have been successful to obtain $YAlB_{14}$ with varying Al occupancy. As a result, excellent control of p-n characteristics (+400 μVK^{-1} to -200 μVK^{-1}) were achieved in a system with same crystal structure and consisting of the same elements.8) Further enhancements of TE properties were obtained by utilizing SPS and doping.9) The surprising discovery of variable metal site occupancy in a boride was also theoretically elucidated.10) A striking "hybrid effect" was also discovered where the conventional TE tradeoff relation was able to be shattered with a 2 order enhancement in electrical conductivity coupled with a 220% increase in Seebeck.11)

(2) Nanostructure control.

Regarding selective phonon scattering, striking effects have been achieved with different methods compared to conventional ballmilling in creating nanoscale interfaces. One is a bottom-up method, where nanosheets of thermoelectric materials were fabricated and achieved a striking low lattice thermal conductivity (lower than amorphous silica glass) without incurring a large penalty in the electrical conductivity.12) In collaboration, an easy mechanical method with room temperature deformation was shown to obtain ultra-low thermal conductivity in bismuth telluride.13)

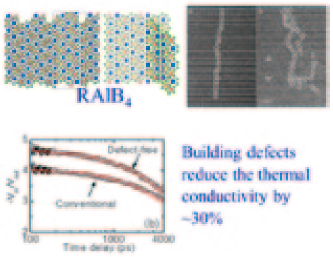

Fig. 1. Controllable nanoscale building defects (top), thermal conductivity (bottom).

(3) Cage compounds for TE .

In collaboration, new clathrate cage compounds with Ge as the network atoms were synthesized and promising TE properties revealed.14,15)

(4) Layered materials and MBE.

With the aim of utilizing building ("tiling") defects recently discovered in layered materials, we have established flux growth methods to control defects in $RAlB_4$ crystals, which are observed by TEM16) and advanced XRD analysis. The nanoscale subtle building defects are indicated to be a mechanism to substantially reduce thermal conductivity (Fig. 1).17) MBE of TE materials with an aim to utilize and definitively prove the "confinement" effect is being carried out for nitrides. For material design, calculations show that 2D AMN_2 layered complex metal nitrides may be superior to the well-known 3D oxides like $SrTiO_3$ (Fig. 2).18)

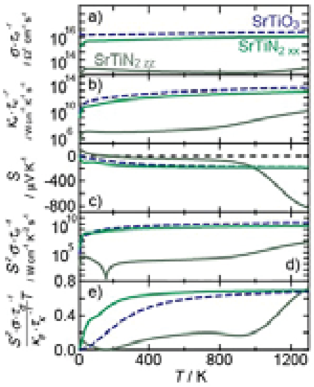

Fig. 2. TE of 2D AMN2.

(5) Other properties (field emission, magnetism).

In collaboration, excellent field-emission performances of NdB_6 nano-needles with ultra-low work functions were observed.19) Unexpectedly strong magnetic coupling was discovered in dysprosium boride insulators $DyB_{22}C_2N$, with the B_{12} icosahedra proposed as a novel mediator of magnetic interaction.20)

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Focusing the Light and Utilize in Nanospace

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

1. Outline of Research

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

When the size of the object shrinks beyond the micrometer scale and when it reaches down to the nanometer or sub-nanometer scale, novel effects that originate from its smallness and its shape come into play.[1, 2] Atom-scale size effects become pronounced especially in metallic objects, since the Fermi wavelengths of metals are in the Ångström range.[1,2] Plasmon polaritons in metal nanostructures show maximum tunability by changing the shape, the size, and thus the dimensionality of the objects. Such feature can be utilized for tailoring optical properties for future nano-photonics/optics devices for information technology as well as high-sensitivity sensors and efficient energy harvesting devices.[2-5]

2. Research Activities

We focused ourselves to the fabrication of various metal-oxide or oxide-oxide nanocomposite materials[6] for the applications in solar energy and heat radiation conversion materials from the ultraviolet (UV) to infrared (IR) spectral region by using both lithographic and self assembly techniques.[1-5] For example, by utilising the electromagnetic field enhancement in metallic nanostructures from the visible to the mid-infrared region the photon energy can be concentrated in nanometer and even down to the subnanometer scale structures.

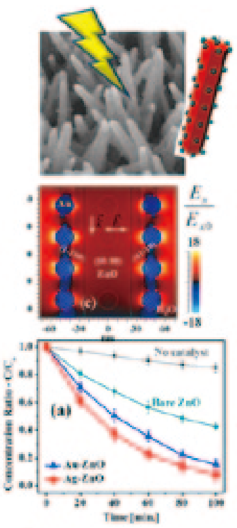

Fig. 1. **An SEM picture of the ZnO nanowires loaded with Au nanoparticles on their surface. (top) An electromagnetic simulation of a Au nanoparticle-loaded ZnO nanowire. (middie) Photodegradation plot of the methylene blue solution irradiated with solar light. (bottom).**

Fig. 1 shows an example of an oxide nanorod and Au nanoparticle composite materials with strong light absorption in the ultraviolet and in visible spectral region. In addition to the enhanced light scattering and optical path length, the highest electric field enhancement is realized in the near field of the Au nanoparticles and the efficient light absorption as well as efficient electron transfer at the nanoparticle/oxide interface is promoted. This would lead to the enhanced photocatalytic activity of this oxide-metal nano-heterostructure in the UV region by the field enhancement and in the VIS region by the hot electron injection as well as by the impurity mediated electron transfer.

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

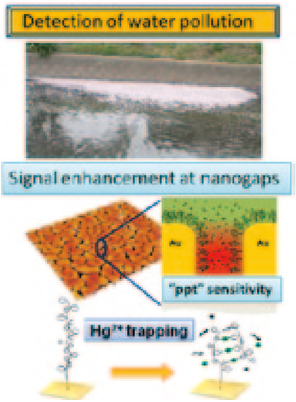

Fig. 2. **Structural change in the aptamer linker molecules caused by the adsorption of Hg^{2+} ions leads to the modification in the optical spectrum. This phenomenon can be utilized for the in situ detection of mercury ions in environmental water.**

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Characterization of Semiconductor Nanostructures by Using EBIC and CL Techniques

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

1. Outline of Research

We 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 cathodo-luminescence (CL) as well as the secondary electron (SE) imaging. First, we have improved the spatial resolution of EBIC/CL by introducing a better electro-optics and optimizing the light collection system. Second, the new specimen preparation techniques, such as cross sectional polisher (CP) and focus ion beam (FIB) have been introduced.

2. Research Activities

(1) EBIC/CL study of GaInAs channel on InP substrate.

Modern computer technology demands a high electron-mobility transistor (HEMT) operating at a higher frequency than that of a conventional Si MOSFET. The i-GaInAs/n-AlGaAs heterojunction is a promising candidate for this electron channel structure for HEMT. However, this heteroepitaxial growth may introduce various crystalline defects, which degrade the performance of the electron channel. We have developed a probe-EBIC system where micro-manipulators are installed in a SEM chamber to drive individual metal probes and form in situ local contact (Fig. 1). This probe-EBIC system enables to study the intrinsic properties of GaInAs electron channel structures and the spatial distribution of electrically active crystalline defects around the structures on the nano-to-macroscopic scale.

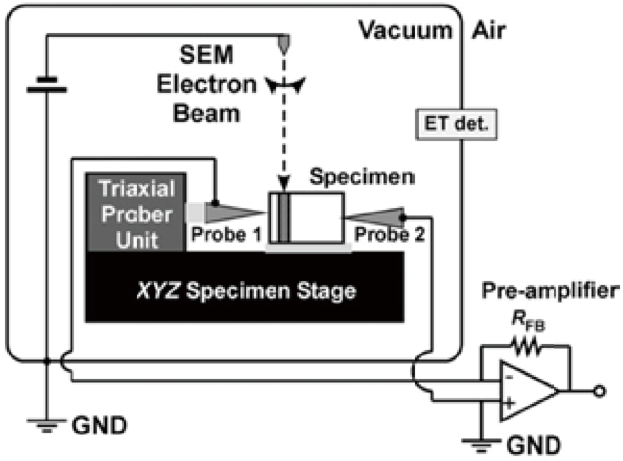

Fig. 1. Schematic of probe EBIC-system.

A cross-sectional secondary electron (SE) and EBIC images of the heterojunction on InP (001) substrate are shown in Fig. 2 (a, b) with an electron beam of 15 keV and 4.4 nA. Apart from the cross-section roughness and related contrasts, there was no dark EBIC contrast around the GaInAs electron channel. This means electrically active defects are not found in this channel area. The combination of CL (c) gives much more information about the band structure of this system.1)

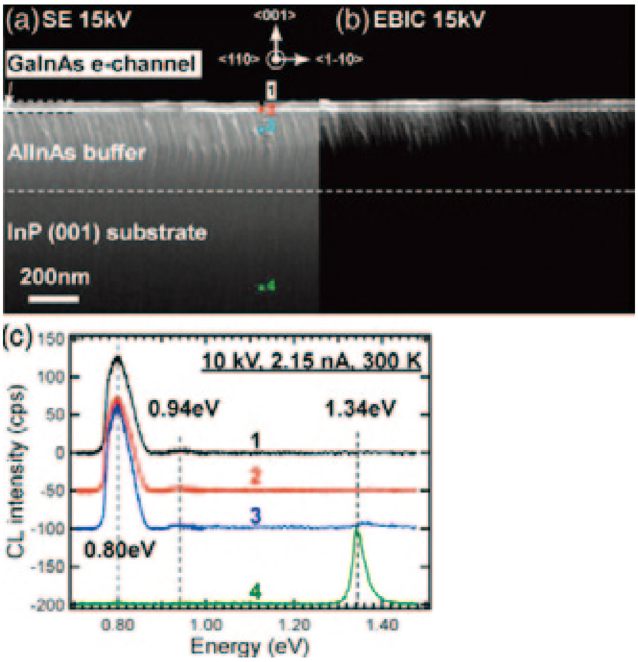

Fig. 2. Cross-sectional SE (a) and EBIC (b) images of GaInAs channel on InP and CL spectra of certain positions.

(2) Modeling of unidirectional growth of Si for photovoltaics (Square-Si).

Although multicrystalline (mc-) Si is a major material for photovoltaic applications, the presence of grain boundaries (GB) decreases the conversion efficiency about 2 % lower than that of mono-Si. Recently, there has appeared high-performance (HP-) mc-Si, which has a better efficiency than that of conventional mc-Si. This suggests the control of GB structure may give another possibility to achieve good efficiency solar cells. Thus, we have developing the model of unidirectional Si growth for the control of GB structure.2)

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Development of Sensor Cells for Nanomaterials Safety Evaluation

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

1. Outline of Research

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

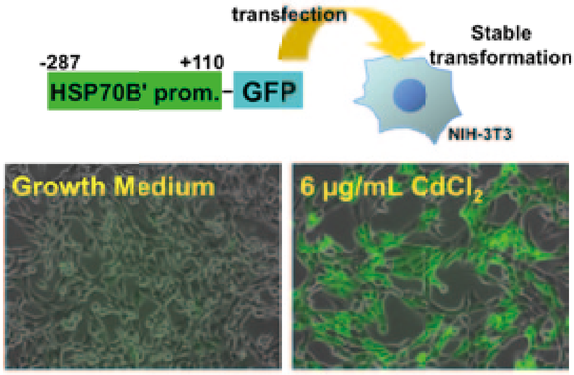

Fig. 1. Construction of sensor cells. Sensor cells were constructed by transfecting plasmids that contain promoter and reporter genes such as HSP70B' and GFP genes in to animal cells.

2. Research Activities

Nanomaterials, expressly nanoparticles, have been manufactured for varied applications. Although they posed a safety risk to our health and environment, recent data have shown the worries concerning their potential toxicity. As we want to develop an effect detection method, how do the nanomaterials affect the cells is important to know. Considering nanomaterials have to be widely synthesized and used for only recent decades, our hypothesis is that there is no enough time for cells to build up specific receptors or signalings for nanomaterials, so the innate cellular defense responses which are against toxins, bacteria, fungi, viruses, and et al., would be used to against the nanomaterials exposure, which we called FHDS. And this FHDS mainly includes inflammatory response, stress response, and genotoxic response. We have fined that toll-like receptor 4 (TRL 4) acted as receptor against nanomaterials (Fig. 2). And so that, three effective sensor cells have been developed, as following: NF-κB sensor cells, which could detect the inflammatory response; HSP70B› sensor cells, which could detect the stress response; BTG2 sensor cells, which could detect the genotoxic response (Fig. 3) and our work could offer some useful information for the interaction investigation between the nanomaterials and cells.[3-7] Moreover, cooperated with different kinds of devices, our sensor cells would be hopeful to be applied for a bio-nanomaterials safety evaluation in the future.

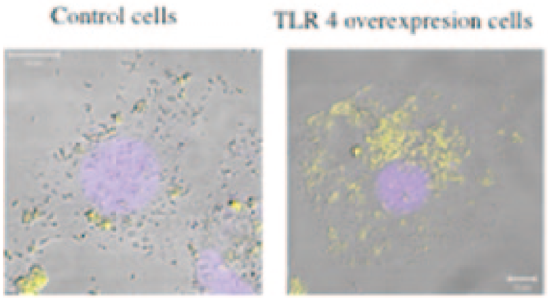

Fig. 2. The uptake of TiO_2 NPs in HepG2 cells in the presence or absence of TLR overproduction.

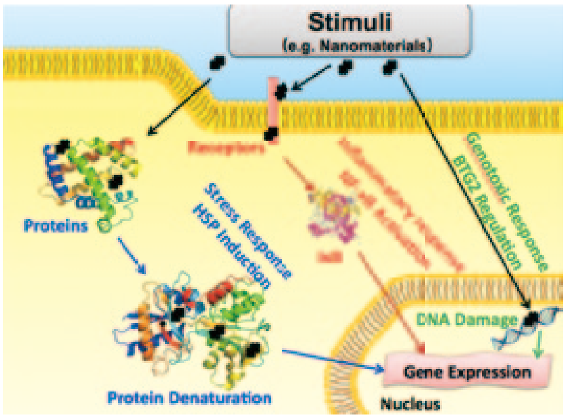

Fig. 3. "First Host Defense System" mainly includes inflammatory response, stress response, and genotoxic response. So that, three effective sensor cells have been developed, recognized by those receptors, and also a "First Host Defense System" response could be induced by the receptors combined with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

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Nano-System Computational Science

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

1. Outline of Research

We are challenging to make novel theoretical frameworks for physicochemical phenomena such as electron transfer, proton transfer & photoexcitation (Fig. 1), since their quantitative calculations are still less established than the conventional techniques for ground state properties.

Our main projects are as follows; (1) development and/or establishment of theories and computational methods for problems in physical chemistry based on the "density functional theory (DFT) and ab-initio calculation techniques", and (2) understanding microscopic mechanisms of elementary reactions in physical chemistry problems by applying these computational techniques. Of particular interest are surface/interface electrochemistry in photocatalysis, dye-sensitized solar cell (DSSC), and Li-ion battery.

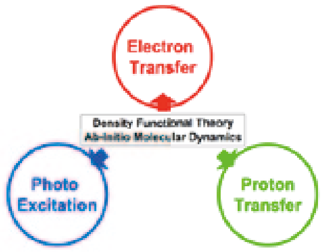

Fig. 1. Research targets in the Nano-System Computational Science group in MANA.

2. Research Activities

(1) New reductive decomposition mechanism of carbonate-based electrolyte in Lithium Ion Battery calculated on the national flagship K computer.[1)]

Solid electrolyte interphase (SEI) on the electrode - electrolyte interfaces formed through the reductive decomposition of organic solvent molecules plays a crucial role in the stability and capability of lithium ion battery (LIB). Additives to the electrolyte often exhibit a large impact on the SEI quality. A typical example is vinylene carbonate (VC) additive to the ethylene carbonate (EC) solvent. Here we investigated the effects of VC additive to the EC solvent on the reductive decomposition and the initial stage of SEI formation.[1)] Our focus was put on kinetics as well as thermodynamics of the possible reduction processes. We used density functional theory based molecular dynamics (DFT-MD) with explicit solvent molecules for the equilibrium properties at finite temperature, and carried out the free energy profile calculations along the reaction pathways using the blue-moon ensemble technique.

We found that 1e reduction induces breaking of C_E-O_2 bond in EC to produce o_E-EC^- and CO, while d_{CO}-VC^- and CO are generated from VC through C_C-O_2 bond breaking in contrast to a previous study (Fig. 2a). When another electron is added to the system (2e reduction), EC decomposition produces CO_3^{2-} + C_2H_4 or CO + alkylcarbonate (Fig. 2b), whereas CO production occurs again at the 2e reduction of VC. We then examined the attack of anion radical made by 1e reduction to the nearby intact molecule, and found that the EC radical attack on the intact VC enhances the CO_2 production. These mechanisms on the atomic scale are in good agreement with the experimental observations of the gaseous products. Contrary to the conventional scenario that VC additive is sacrificially reduced and makes a VC oligomer that seeds SEI formation, the present results provide a completely different mechanism: the VC additive preferentially reacts with the EC anion radical to suppress the 2e reduction of EC, the main initial stage of SEI formation in the VC-free EC electrolyte (Fig. 2c). Because this VC mechanism is realized via 1e reduction, the irreversible capacity at the SEI formation will decrease as well, which is also consistent with the experiments. These results not only reveal the primary role of the VC additive in the EC solvent, but also provide a new fundamental perspective for the reductive decomposition of carbonate-based electrolyte near the negative electrode.

(2) Mechanism prediction with DFT simulations on unusual phenomena observed in experiments.[2-4)]

With large-scale DFT simulations on supercomputers, we have predicted the mechanisms of unusual swelling of nanosheets with specific electrolyte, unusual high mobility of hole in special organic crystals, and a novel type of molecular switch.

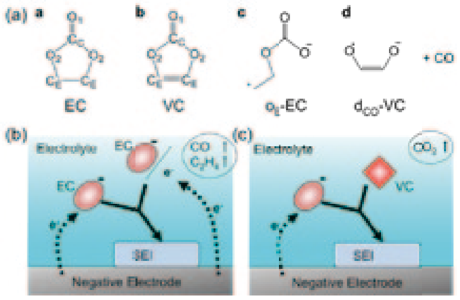

Fig. 2. (a) Structures of EC and VC with the atomic labels. Major reductive decomposition products of EC and VC (oE-EC and dCO-VC) are also displayed. (b) Reductive decomposition mechanism for the electrolyte with EC only, confirmed in this work. (c) Novel reductive decomposition mechanism of the EC electrolyte with VC additives, found in this work.

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All-Solid-State Electric-Double-Layer Transistor Achieved by Oxygen Ion Migration

Group Leader (Nano-System Field) **Kazuya TERABE**
MANA Research Associate Takashi Tsuchiya

1. Outline of Research

The fine processing scale for the conventional semiconductor device will reach the atomic scale in near future. It is evident that not only the limits to conventional fine processing technology but also the physical operating limits of semiconductor devices are being reached. One possible way to overcome these technological and physical limits of the existing conventional semiconductor device is to achieve breakthroughs in nanotechnology materials and novel device-operation principle. A promising type of such nano-devices is the nano-ionics device,[1] which is operated by controlling the local ion migration and electrochemical reaction instead of electron and hole migration.

Electrostatic modulation of the electronic carrier in solid materials is an interesting technique for developing the novel nano-device. The attractiveness lies in the ability to easily control the electronic carrier density merely by adjusting the dc bias voltage and in the freedom from the structural disorder inherent in chemical doping. Unfortunately, the maximum carrier density obtained for solid dielectric material is smaller than 10^{13} cm^{-2} due to the low dielectric constant and low breakdown voltage. Recently, an electric double layer (EDL) using liquid electrolytes has been used to overcome these limitations, and a much higher carrier density of 10^{14} cm^{-2} has thereby been attained.[2] However, the non-solid-state electrolytes including the ionic liquid or ion conducting gel have serious problems in compatibility with other electronic devices.

In our study, we have succeeded to develop an all-solid-state EDL transistor based on oxygen ion migration in a solid electrolyte. While the response speed of an EDL transistor is far below that of a modern field-effect transistor due to the slow diffusion of ions, the all-solid-state EDL transistor enable compatibility with conventional semiconductor device, and has potentially useful for creating unique nano-devices with new functionalities.

2. Research Activities

We used a Gd-doped CeO_2 (GDC) thin film of oxygen ion conductor deposited on $SrTiO_3$ (STO) single crystal to explore the feasibility of an oxygen-ion all-solid state EDL transistor.[3] The GDC material is well known as a good and pure oxide-ion conductor due to the formation of oxygen vacancy, which maintains the electroneutrality. The proposed all-solid-state EDL transistor, schematically shown in Fig. 1, was fabricated on an atomically flat (001) surface of STO single crystal. A 400-nm-thick GDC thin film was deposited by pulse laser deposition. All source, drain, and gate electrodes were made of Pt and deposited by RF sputtering. Aluminum thin films have been inserted to eliminate Schottky barriers at source/STO and drain/STO interfaces. The electrical conduction of the transistor was characterized by using a variable temperature three-probers station.

The electrical conduction characterization of the STO-based EDL transistor reveals that while its operation temperature is limited to above 400 K, the use of oxygen ion gating resulted in a large resistance change (four orders of magnitude) and a capacitance of 14 μF cm^{-2}, which is equivalent to a two-dimensional carrier density of 10^{14} cm^{2} for a V_{gs} of 3 V. The huge capacitance at the GDC-based interface, comparable to that of the liquid electrolyte EDL transistor and its strong dependence on the electrode property indicates that a combination of GDC with other insulators and semiconductors should produce outstanding performance. This device offers not only high carrier density but also excellent compatibility with a wide range of electronic devices owing to its all-solid-state configuration needing no absorbed water molecules. The door has thus been opened for controlling various physical properties by means of nanoionic motion in solid materials.

We believe that the developed approach of the integrating ionics and electronics on the nanoscale should lead to breakthroughs in the development of a wide range of future nano-devices.

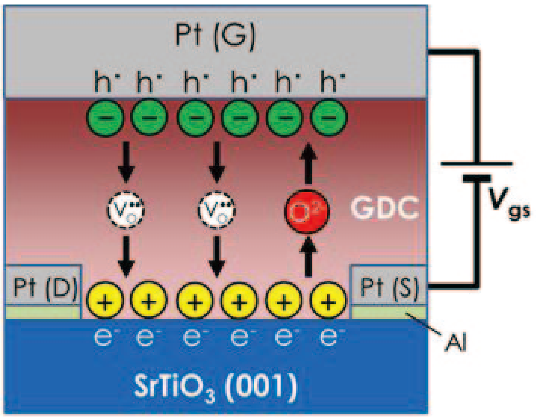

Fig. 1. **Schematic illustration of STO-based EDL transistor using a solid electrolyte of GDC oxygen ion conductor and STO single crystal. Yellow and green circles represent positive and negative charges accumulated at interfaces by oxygen ion and vacancy migration. O^{2-} and Vö are negative oxide ions and positive oxide ion vacancies, respectively.**

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Cytocompatibility of Mg Alloys and the Effects of Cells on their Biodegradation

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

1. Outline of Research

Magnesium and its alloys are expected as bioabsorbable metals in the biomedical field since they are easily corroded by reacting with water in the body fluid. However, excess generation of OH$^-$ accompanying the corrosion reaction increases pH of the fluid, which inhibits cell growth on the sample surface. Therefore, the cytocompatibility of Mg alloys depend on the balance of their corrosion rate and the diffusion rate of generated OH$^-$ by blood flow. However, no standard method has been established to evaluate cytocompatibility of Mg alloys.

In this study, a new cultural condition is applied for cytocompatibility evaluation of Mg alloys, considering the environment in the human body. The amount of culture medium is set as 1/100 of blood plasma in a adult human since it significantly influences the corrosion rate of Mg alloys as well as its resulting pH. As model substrates, Mg-Al-Zn alloys, which are commonly used in industries, are employed to demonstrate this new cultural condition can detect the difference in their cytocompatibility.

2. Research Activities

The materials used are commercially available extruded bars of pure Mg (pMg), Mg-3wt.%Al-1wt.%Zn (AZ31), Mg-6wt.%Al-1wt.%Zn (AZ61), and Mg-8wt.%Al-0.5wt.%Zn (AZ80) alloys. For all alloys, the top surface of a sample is a cross section to the extrusion direction.

The results of cytocompatibility tests using murine fibroblast L929 are shown in Fig. 1 (left).[1] Good cell growth was observed on pMg and AZ31 along the incubation period, whereas almost no growth was observed on AZ61 and AZ80. Mg^{2+} release from the samples during cell culture is also summarized in Fig. 1 (right).[1] The highest Mg^{2+} release after cell culture was observed from pMg, followed by AZ31, AZ61, and AZ80 in the order, corresponding inversely to the Al content in the alloys. Mg-Al-Zn alloys are well known to improve their corrosion resistance with the increase in their Al content. These facts indicate that the low cell growth on AZ61 and AZ80 is not caused by the pH increase of the medium due to their corrosion reaction.

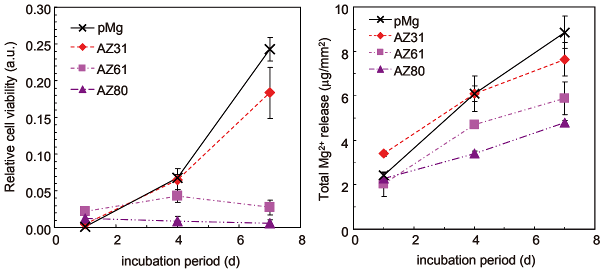

Fig. 1. **Cytocompatibility tests of pMg, AZ31, AZ61, and AZ80 with L929 cells (left) and total Mg^{2+} release during the tests (right).**

Mg^{2+} release from the pMg and AZ31 samples with and without cells during the incubation up to 7d is shown in Fig. 2.[1] For both materials, the samples incubated with cells tended to have slightly higher Mg^{2+} release than those from the samples immersed without cells. This data suggests that the existence of cells accelerates the degradation of Mg alloys, which is probably due to the slightly lower pH of the medium by the metabolic activity of the cells. The same trend was observed by the electrochemical impedance spectroscopy of Mg-Ca alloy samples under the cell culture condition.[2]

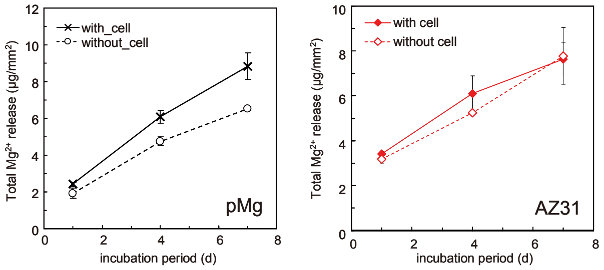

Fig. 2. **Mg^{2+} release from pMg and AZ31 with and without cells during the incubation upto 7 d.**

Protein adsorption onto a material surface controls following cellular adhesion and response. Therefore, albumin and fibronectin adsorption behavior was examined as shown in Fig. 3.[1] The tendency of fibronectin adsorption onto pMg and AZ31 corresponds to the cell growth after 7d incubation. However, suppression of cell growth on AZ61 and AZ80 could not be explained by the protein adsorption behavior on these surfaces. Higher Al concentration at the surface, which is confirmed by the EDX analysis of the sample surfaces after cell culture, is supposed to be related, but further investigation is necessary to elucidate actual cause and its mechanism to suppress cell growth on high-Al-content Mg alloys.

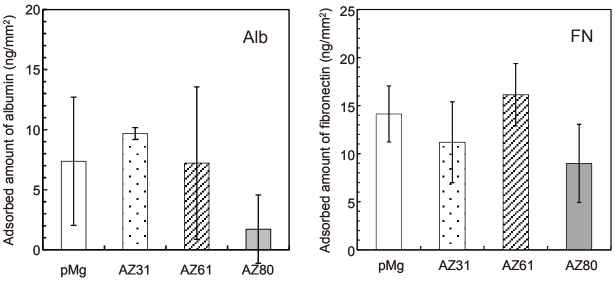

Fig. 3. **Absorbed amount of proteins onto pMg, AZ31, AZ61 and AZ80 after 3h of immersion into protein-artificial plasma solution.**

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Laser-Based Inelastic Photoemission Spectroscopy

MANA Independent Scientist Ryuichi ARAFUNE

1. Outline of Research

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

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

2. Research Activities

(1) Angle resolved inelastic photoemission spectroscopy.

To develop a novel vibrational spectroscopic technique based on this inelastic phenomena and to gain a deeper understanding of the process, we have measured the inelastic photoemission spectra of the CO covered Cu(001) surface. For this purpose, we have constructed a laser-based photoelectron spectroscopy system equipped with a two-dimensional CCD camera detector. At normal emission, the photoelectron spectra excited by the low energy laser photon ($h\nu$ = 4.80 eV, T=7.6 K) contain the inelastic structures arising from the excitation of the frustrated translational (FT) and frustrated rotation (FR) mode. Since the energy shift for the FT mode (i.e. the vibrational energy) is low (~ 5 meV), we cannot measure its angle dependence. On the contrary, the inelastic component for the FR mode shows a very small but systematic dependence on the emission angle (~ -1meV/7 degree). We conclude that this angle dependence of the inelastic component originates from the phonon dispersion of the FR mode. These results demonstrate that the angle resolved inelastic photoemission spectroscopy is a useful tool for measuring the dispersion relation of the low-energy vibrational mode.

(2) Investigation of mode-selectivity in inelastic photoemission process by using Density functional perturbation theory.

The simplest system in which the characteristic inelastic feature appears in LPES spectra is Cu(110). In order to gain the insight, we carried out the theoretical calculations for the electronic state and surface phonon modes on Cu(110) based on the density functional theory (DFT) and density functional perturbation theory (DFPT). From the calculation results of electronic and phonon band structure and electron-phonon coupling, we conclude that the source of inelastic feature on Cu(110) is the photoelectron-phonon interaction at Y point of surface Brillion zone. What is more, we found that the phonon modes which strongly coupled to photoelectron at Y point are distributed between subsurface and bulk region. These results indicate the possibility of LPES as a novel technique to detect phonon at subsurface and deeper region.

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

Carbon and silicon are members of the 14th group in periodic table. There exist several allotropes of C such as graphite, diamond and amorphous carbon whereas the allotrope of Si corresponding to the graphite does not exit in nature. Silicene, two-dimensional honeycomb sheet consisting of Si atoms, is a allotrope of Si and attracts much attention as a new low-dimensional material because it is predicted theoretically to show many fascinating properties originating from the combination of Dirac fermion features with the large spin-orbit coupling. In particular, the novel properties such as quantum spin Hall effect and the compatibility with the current Si device technologies triggers the competition to realize the silicene. Recently, silicene has been synthesized on several different substrates. We have succeeded in determining the geometric and electronic structure of silicene on Ag(111) substrate by combination of scanning tunneling microcopy (STM), low energy electron diffraction (LEED) and the density functional theory (DFT) calculations.

Search for New Ferroelectric, Magnetic, and Multiferroic Materials Using High-Pressure Technique

MANA Independent Scientist Alexei A. BELIK

1. Outline of Research

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

Among different multiferroic materials, spin-driven multiferroics attract special interest because ferroelectricity is induced by magnetic ordering and, therefore, the coupling between different order parameters is usually very strong. Ferroelectric and dielectric properties can easily be controlled by magnetic fields in such spin-driven multiferroics. Spin-driven ferroelectricity appears from spin frustration, in general, or more specifically from spiral and cycloid spin orders, exchange striction, and spin-direction dependent metal-ligand hybridization.

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

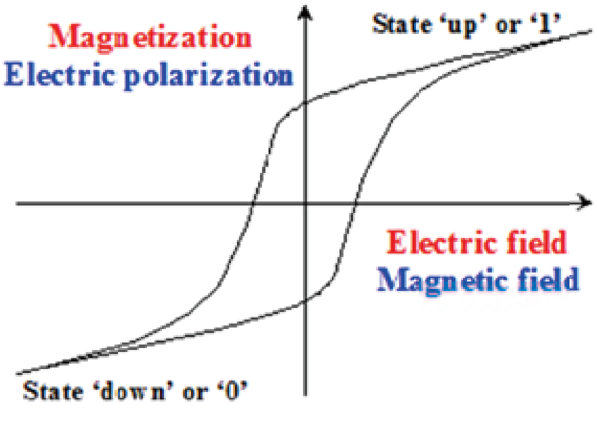

Fig. 1. Ferroelectric/ferromagnetic hysteresis loop: the basis of many memory elements.

2. Research Activities

(1) New Spin-Driven Multiferroics Sc_2NiMnO_6 and In_2NiMnO_6.[1)]

'Usual' perovskite-type compounds with the general formula ABO_3, where A is La-Lu, Y, and Bi and B is V, Cr, Mn, Fe, Co, Ni, and Cu have been attracting a lot of attention for decades. 'Exotic' perovskites are also highly interesting because new phenomena may emerge in them. The term 'exotic' may include compounds with unusual oxidation states, unusual ion distribution, and unusual ions at the A site and B site. Perovskites with A = Sc and In have small tolerance factors, and they can be prepared only at high pressure. We investigated in details properties of Sc_2NiMnO_6 and In_2NiMnO_6. They have antiferromagnetic ground states in comparison with the ferromagnetic ground state in the R_2NiMnO_6 (R = Y and La-Lu) family. Sharp dielectric anomalies were observed at their magnetic ordering temperatures indicating that they are spin-driven multiferroics. Magnetic fields have strong effects on their dielectric properties.

(2) The origin of the mystery of negative magnetization in perovskite materials.[2,3)]

Some perovskite materials exhibit the magnetization reversal (MR) or negative magnetization effect. MR was originally predicted and observed in some ferrimagnets having several magnetic sublattices due to different temperature dependence of sublattice magnetizations. However, the origin of MR in perovskite-type compounds with one magnetic sublattice is still a matter of debate in the literature. Different explanations have been proposed. We suggested that 'positive exchange bias', 'defects', 'interfaces', and 'pinning' should be keywords for understanding MR in addition to or instead of 'single-ion magnetic anisotropy' and 'Dzyaloshinsky-Moriya interaction' keywords; and a general fundamental question should be: 'what are the origin and mechanism of exchange bias in (seemingly) single-phase and homogeneous materials?'

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Photoisomerization–Induced Manipulation of Single-Electron Tunneling in Si-Based Devices

MANA Independent Scientist Ryoma HAYAKAWA

1. Outline of Research

The evolution of complementary metal-oxide-semiconductor (CMOS) devices is now reaching a major turning point owing to the critical limit imposed by increasing large-scale integration and growing power consumption. Single molecular devices such as single molecular transistors and memories have been promising candidates for realizing "beyond CMOS" devices.[1] However, the development of such molecular devices is still at the basic research stage and practical application remains a long way off. The main obstacle is the lack of effective device structures for molecular devices. For this purpose, we have proposed the adoption of functional organic molecules as quantum dots in a single-electron transistor and memory.[2] Here, we consider organic molecules to be excellent quantum dots compared with their inorganic counterparts. First, the molecules have a uniform size on a nanometer scale thus achieving quantum dots with a large number density. The number density of the molecules can reach around 10^{13} cm^{-2}, which is two orders of magnitude higher than that of inorganic dots ($\sim 10^{11}$ cm^{-2}). Another advantage of the molecules is the tunability of the molecular orbitals. Specifically, photochromic molecules, such as diarylethene and azobenzene molecules, permit the molecular orbitals to be reversibly changed by light irradiation.[3] That is, the carrier injection can be manipulated by alternating external triggers, namely light irradiation and gate voltage. This is a unique feature of organic molecules that makes them very different from inorganic dots.

2. Research Activities

(1) Change in molecular vibrations with light irradiation.

A derivative of diarylethene molecules, 1,2-bis(2-methyl-5-(4-biphenyl)-3-thienyl)hexafluorocyclopentene, was employed in the form of optically controllable quantum dots. First, attenuated total reflection (ATR) Fourier transform infrared (FT-IR) spectroscopy measurements were performed in samples with Al_2O_3/diarylethene thin film/SiO_2/Si multilayer structures to provide clear evidence that the diarylethene molecules undergo photoisomerization even in insulator layers.

Fig. 1a shows ATR FT-IR spectra of diarylethene thin films embedded in the insulator layer with alternating visible (VIS) and ultraviolet (UV) light irradiation. Characteristic vibration peaks in the diarylethene molecule were observed in spectra (i) and (ii), for instance, C=C and C-C stretching vibrations in phenyl and thienyl ringsand C-F stretching vibrations in hexafluoro-cyclopentene rings. Moreover, the peak intensity of the C=C vibration at 1483 cm^{-1} in difference spectra (iii) was reversibly changed by alternating UV and VIS light irradiation (Fig. 1b). These results clearly show that the photoisomerization of diarylethene molecules appeared even in insulating layers.

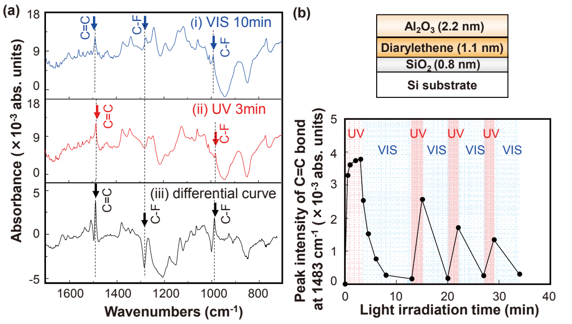

Fig. 1. (a) ATR FT-IR spectra of a diarylethene film with (i) VIS or (ii) UV light irradiation and (iii) a difference spectrum. (b) Change in peak intensity (C=C bond) in differential spectra for irradiation time.

(2) Optical manipulation of single-electron tunneling in Si-MIS structure.

Fig. 2 shows current-voltage (*I-V*) curves under UV or VIS light irradiation in an ITO/Al_2O_3/diarylethene molecule/SiO_2/Si multilayer measured at 20 K. Here, the 3.2 nm-thick Al_2O_3 and 1.2 nm-thick SiO_2 thin films serve as tunneling barrier layers. Before the measurement, the sample was irradiated with visible light for 10 min to elevate the open-ring to closed-ring isomer ratio. Multiple staircases were seen in the *I-V* curve. The result clearly indicates that each diarylethene molecule works as a quantum dot for single-electron tunneling (SET).

Then, the threshold voltages of SET were changed by alternating UV and VIS light irradiation along with photoisomerization of diarylethene molecules. First, the threshold voltage was reduced after UV light irradiation for 2 min. After that, VIS light irradiation for 5 min induced a reversible change to a higher voltage. In this manner, the reversible variation in the threshold voltage was repeatedly observed at several times by alternating the UV and VIS light irradiation. These results show that the diarylethene molecules can work as optically controllable quantum dots in a practical Si device configuration.

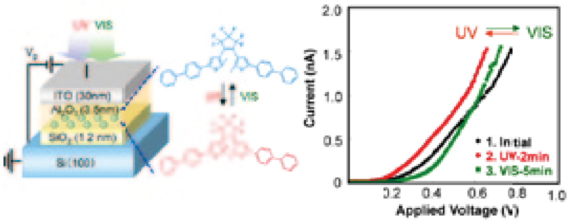

Fig. 2. Optical manipulation of single-electron tunneling in the samples with diarylethene molecules as quantum dots.

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Oriented Assembly of Plasmonic Nanoparticle Clusters for SERS Sensing

MANA Independent Scientist Joel HENZIE

1. Outline of Research

Shaped colloids can be used as nanoscale building blocks for the construction of composite, functional materials that are completely assembled from the bottom up.[1] Assemblies of noble metal nanostructures have unique optical properties that depend on key structural features requiring precise control of both position and connectivity spanning nanometer to micrometer length scales. Identifying and optimizing structures that strongly couple to light is important for understanding the behavior of surface plasmons in small nanoparticle clusters, and can result in highly sensitive chemical and biochemical sensors using surface-enhanced Raman spectroscopy (SERS).

2. Research Activities

(1) Hierarchical self-assembly of polyhedral plasmonic clusters.[1,2]

Hierarchical assembly is used to guide particles into the desired arrangements. We developed a method reminiscent of gravure printing, where a solution of nanoparticles is drawn over a patterned surface, and particles are deposited in recessed regions. This method can produce large-area patterns of metal particles with a low rate of defects. We demonstrated reproducible, well-defined clusters with strong single SERS enhancement factors (SSEFs) at a range of excitation wavelengths (Fig. 1) including 633 and 785-nm.

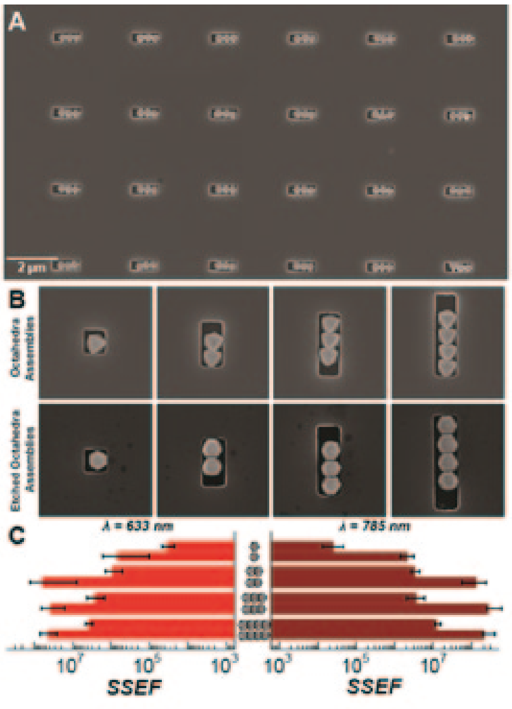

Fig. 1. Large-scale assembly of particles into linear and circular templates. (A) SEM image of an array of octahedra trimers in identical-sized pits in Si. Measuring these arrangements side-by-side enables interrogation of SERS enhancement of each trimer under identical excitation conditions. (B) SSEFs at λ_{ex} = 633 and 785 nm for single particles, dimers, trimers, and tetramers composed of octahedra and mildly etched octahedra.

(2) Modeling the optical properties of nanoparticle clusters.

To understand how the structure of dimer nanoparticle clusters affects optical properties and SERS enhancement, we used electromagnetic (EM) modeling tools to examine their near field optical properties. Fig. 2 shows a rendering three types of dimers, with a red plane in the gap and normal to the long axis. These dimers scatter light at broad wavelengths, but here we show the SERS spectrum of 4-aminothiophenol (4-AMT) (left) and EM field maps (right) using light excitation at λ = 785 nm. This work has allowed us to develop new kinds of SERS sensors with higher sensitivities that should eventually approach the single-molecule level.

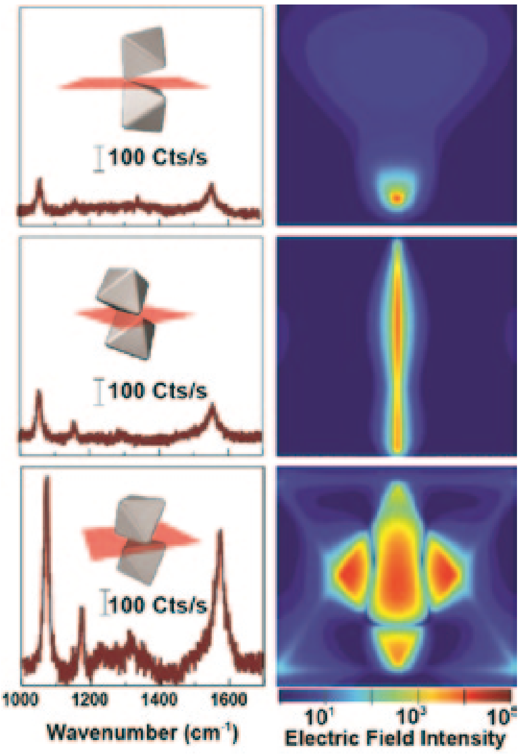

Fig. 2. SERS properties and near-field enhancement of dimers at different excitation wavelengths. Representative SERS spectra of (4-AMT) and near-field electric field intensity maps corresponding to the SERS excitation wavelengths (λ) and the specified Stokes modes of 4-AMT for the different arrangements of octahedra dimers. All near-field intensity maps use the same color bar below.

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Printing of Functional Inks for High Performance Thin-Film Devices

MANA Independent Scientist Takeo MINARI

1. Outline of Research

Recent developments in electronic devices offer dramatic improvements in the conveniences of daily life, while at the same time causing destruction of the environment and exhaustion of natural resources. Current production processes for semiconductor electronic devices require huge conveyer lines and large-scale equipment operating under clean conditions, and these top-down technologies result in a substantial waste of materials. These factors also increase production costs and investment in facilities. Thus, the solution-based, bottom-up fabrication methods with minimal consumption of energy and materials are required.[1)] We have developed a fabrication method of fully-printed organic field-effect transistors (OFETs), which offers large-area, low-cost fabrication of flexible electronic products.

2. Research Activities

(1) A plastic model painted in real gold.

Gold is one of important colors for painting. However, a conventional gold ink is actually a composite of silver and yellow, and use of real Au is limited. Here we developed a method which allows us to use real Au as the ink for painting. We chose the plastic model, Zaku-II, as the curving substrate (Fig. 1). The Au nanoparticles (NPs) having room-temperature processability is offered by Prof. Kanehara (Okayama Univ.). Since the surface of a plastic is hydrophobic, we introduced a surface modifying layer using the spray deposition technique to improve the adhesion of Au NPs to the surface. The solution of Au NPs was applied simply using a painting brush. This simple process enables the modification of the material surfaces by real Au.

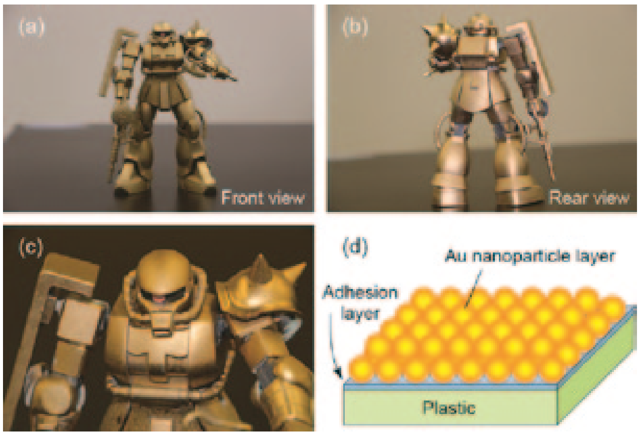

Fig. 1. A plastic model painted in real gold. Front view (a) and rear view (b) of the plastic model. (c) A magnified image of the plastic model. (d) Schematic illustration of the plastic surface modified with gold nanoparticles.

(2) Printing of high-mobility OFET arrays.

In current printed electronics, processes conducted at temperatures greater than 150 °C typically are used, which prevents use of a common flexible substrate because of the distortion caused by heat. We significantly lowered the fabrication temperature of printed electronics products using the novel Au NPs as the electrode material. Low-temperature patterning methods also were developed for an active organic semiconductor layer, which enables accurate stacking of four layers for formation of OFETs through printing. The fully-printed OFET devices exhibited average field-effect mobilities of 7.9 and 2.5 cm^2/Vs on plastic and paper substrates, respectively (Fig. 2). These results suggest that this fabrication method is very promising as a core technology for low-cost and high-performance printed electronics.[2)]

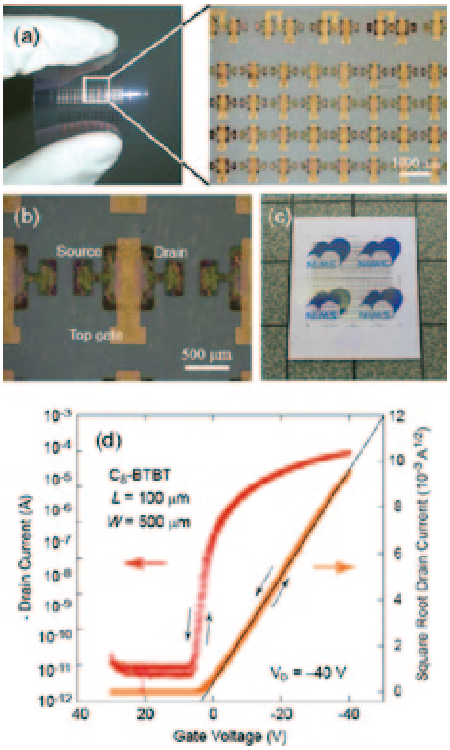

Fig. 2. Fully-printed OFET devices fabricated on a plastic substrate. (a) Flexing the printed OFET arrays on the plastic substrate (left). Substrate size was 40 × 40 mm^2. An optical microscope image of the OTFT array (right). (b) An optical microscope image of the individual device. The electrode and organic semiconductor layers are fully patterned to reduce the off current and cross-talk among the devices. (c) An OFET array printed on the paper substrate. The size of the paper was 40 × 50 mm^2. (d) Typical transfer characteristics of the OFET device.

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Quantum Transport in Nanostructured Materials

MANA Independent Scientist Satoshi MORIYAMA

1. Outline of Research

A quantum dot is a small metallic island with a single electron charging effect and zero-dimensional confined states, which resembles to the natural atom. For this reason, the quantum dot is often called an artificial atom. Although the atom-like physics is studied their interaction with light, artificial atoms can measure electron transport properties in solid state systems. Therefore, quantum dots are expected for future electric devices that can control the single-electron charge and spin states. The quantum computing devices which may use both the single electron effect and the quantized level need quantum coherence as well. Based on the above background, we explore novel quantum-dot devices that have different functions with conventional transistor. As the working temperature of these devices is directly related to the size of their island, they have motivated the study of transport properties through novel nanostructured materials.

2. Research Activities

(1) Ultra-thin Gold Nanowires as Quantum Dots.[1]

Recently, ultra-thin gold nanowires (AuNWs) with a diameter of a few nanometers have been produced by wet chemical synthesis. These AuNWs, which are difficult to realize with conventional lithography techniques, could be promising candidates for nanowire-based single-electron devices following carbon nanotubes and semiconductor nanowires. In addition, it might be possible to apply AuNW-based QDs to single-electron spintronic devices by taking advantage of the large spin-orbit coupling in heavy metal elements such as gold. We show the electron-transport data of an individual ultra-thin AuNW, which exhibits Coulomb blockade effects and spin splitting of single-particle states in magnetic fields.

Several techniques have been used to synthesize AuNWs in the last decade, and we employed wet chemical synthesis. The synthesized AuNWs were about 2 nm thick and up to 1 μm long and were coated with a layer of oleylamine as a surfactant. The AuNW devices were fabricated on a highly doped silicon substrate with a SiO_2 top layer that was used as a back-gate insulator. Source and drain electrodes were patterned on the substrate. Then, a few droplets of the solution containing the AuNWs were drop-cast onto the substrate to connect the AuNWs to the electrodes. The electrical contact between an AuNW and an electrode was formed through a layer of oleylamine, which functioned as a tunnel barrier. The electrical transport at low temperatures revealed single-electron transport characteristics, and the spin splitting of single-particle levels was observed in magnetic fields.

(2) Superconductivity in Niobium-Nitride Nanowires on Suspended Carbon Nanotubes.[2]

Superconducting nanowires are attractive for the low-dimensional transport study, as well as for future quantum nanodevices, such as single-photon detector and quantum phase-slip qubits. Recently, free-standing carbon nanotubes as nanowire templates for material deposition has been developed. We show experimental results on the one-dimensional (1D) superconductivity in nanowires produced by coating suspended carbon nanotubes with a Niobium-Nitride (NbN). We prepared the Si substrate with a 120 nm SiO_2 layer, where slits were patterned by electron beam lithography and dry etching (the width of the slit are ranging from 1 to 5 μm). The Si layer under the slits was further removed by dry etching, which leads to an undercut structure. This undercut guarantees the electrical disconnectivity between electrodes across the trench. The CNTs were grown by chemical vapor deposition and they are suspended over the slits, on which NbN was sputtered. The wire width (W) of the NbN nanowires takes values of 10 - 130 nm, as estimated from the deposition time and the scanning electron microscope images.

All electrical transport measurements are carried out at low temperatures from 5 K to 20 K. The wire width 10 nm nanowire shows the superconductor-insulator transition, and 25 nm nanowire begins to show the superconducting fluctuation. From the resistance-temperature (R-T) characteristic curves, the signatures of the 1D superconductivity with phase-slip events are observed in $W > 25$ nm nanowires. Fig. 1 shows the bias-current dependence of the R-T characteristic curves. A high bias current induces a set of discrete and quantized resistance drops, which becomes more evident as the bias current is increased. Some resistive steps occur at the same temperature regime as has already been reported in classical papers on tin whiskers and it should be identified with phase-slips due to sample inhomogeneities.

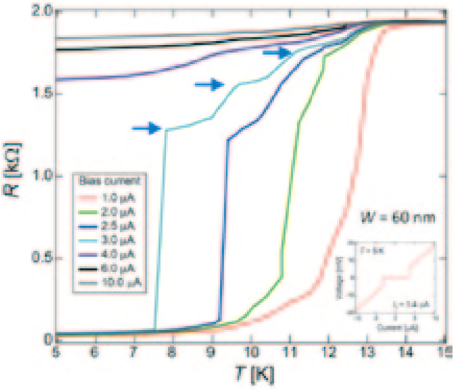

Fig. 1. Bias-current dependence of the R-T characteristics at W = 60 nm NbN nanowires.

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Development of Photoresponsive Biointerfaces

MANA Independent Scientist Jun NAKANISHI

1. Outline of Research

Biointerface is an interface between biomolecules and materials. It plays a pivotal role in biomedical devices such as materials for drug delivery, tissue engineering, and bioanalysis. The major purpose of the present study is to develop chemically functionalized biointerfaces with photochemically active compounds and apply them for analyzing and engineering cellular functions (Fig. 1).[1-3]

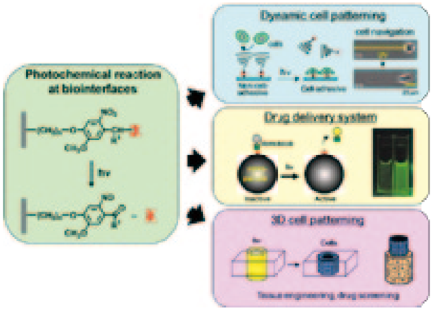

Fig. 1. Photoresponsive biointerfaces developing in this study.

2. Research Activities

(1) A photoactivatable nanopatterned substrate for analyzing collective cell migration with precisely tuned cell-extracellular matrix ligand interactions.

Collective cell migration plays critical roles in both physiological and pathological processes. Basically, epithelial cells migrate collectively, whereas mesenchymal cells prefer to migrate as individuals. However, in some spatiotemporally limited situations of life, some cells aggressively ignore this rule. For example, the change in the collective characteristics via epithelial-mesenchymal transition (EMT) or vice versa (MET) is essential in embryonic development and morphogenesis. Also, cancer metastasis can be considered as the loss of the collective feature upon escaping from the original tissue and its retrieval to settle down and form new colony at other tissues. So far, various internal and external factors have been shown to change collective characteristics in vitro and in vivo, however most of which were focusing on soluble factors or oncogenes, and less attention was paid for the contribution of cellular niches, composed of surrounding cells and extracellular matrices (ECMs), on the regulation processes.

To tackle this issue, we developed a method for analyzing collective cell migration with precisely tuned cell-ECM ligand interactions (Fig. 2).[4] Gold nanoparticles are arrayed on a glass substrate with a defined nanometer spacing by block copolymer micellar nanolithography (BCML), where photocleavable poly(ethylene glycol) (Mw = 12 kDa, PEG12K) and a cyclic RGD peptide, as an ECM ligand, are immobilized. The remaining glass regions are passivated with PEG2K-silane to make cells interact with the surface via the nanoperiodically presented cyclic RGD ligands upon photocleavage of PEG12K. On this nanostructured substrate, HeLa cells are first patterned in photo-illuminated regions, whereas cell migration is induced by a second photocleavage of the surrounding PEG12K. In contrast to a homogenous substrate, HeLa cells gradually lose their cell-cell contacts and become disconnected on the nanopatterned substrate with 10-nm particles and 57-nm spacing. Interestingly, the relationship between the observed migration collectivity and the cell-ECM ligand interactions is opposite from what expected from conventional soft matter models. It is likely that the reduced phosphorylation on tyrosine-861 of focal adhesion kinase (FAK) on the nanopatterned surface is responsible for acquiring this unique migration behavior. The results represent usefulness of the presented method for understanding the determination process of collective/non-collective migration features in defined micro- and nano-environments, as well as for resolving crosstalk between cell-cell and cell-ECM adhesions. These results verify the usefulness of the presented material-based approach in exploring cellular nanoarchitectonics in collective cell migration, which will be complementary to conventional molecular biological methods.

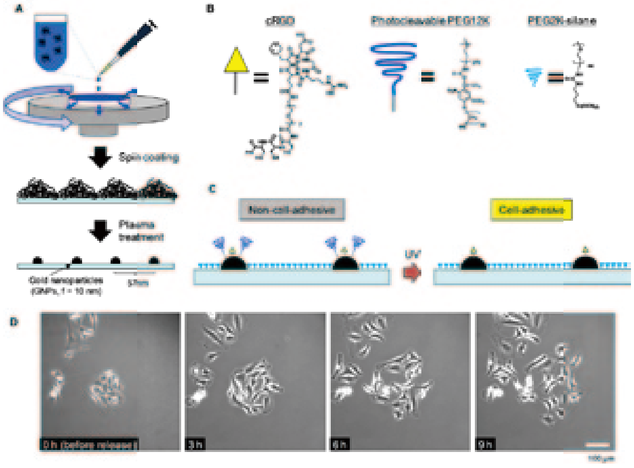

Fig. 2. Schematic drawing of a photoactivatable nanopatterned substrate and unique non-collective motion of HeLa cells on the nanopatterned surface.

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Green Nanochemistry: Bandgap Engineering for Group IV Nanostructures

MANA Independent Scientist Naoto SHIRAHATA

1. Outline of Research

Findings of strong luminescence from nanostructures of group IV semiconductors and their compounds, i.e., Si, Ge, Si_xGe_{1-x}, and silicide, have generated a great deal of excitements because their light emitters have a potential to open a new door to silicon photonics. Furthermore, the industrial use of 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 sustainable future.

2. Research Activities

*(1) Continuous tuning of emissions in the NUV-VIS-NIR range.*1)

This paper reviews a series of representative synthesis processes which have been developed in the last two decades to prepare silicon nanoparticles (npSi) of either one of various forms including crystals and clusters. Photophysical properties of npSi are highlighted to report the continuous tuning the color of fluorescence in a wide emission ranging from near-UV (NUV) through full color of visible to near-IR (NIR, Fig. 1). Interestingly, the tuning ranges of emissions are strongly dependent of methodological approaches. A diamond cubic lattice of Si is commonly produced at high temperature. Subsequent acidic etching is used for size-reduction of the crystalline Si. According to spectroscopic study, most of ncSi with diamond cubic lattices emit the lights in the NIR region or VIS (longer than 570 nm) region. The npSi emitting the light shorter than 570 nm have been mainly synthesized by solution processes. The processes include electric reduction of molecular silicon halides under mild conditions and laser ablation at ambient conditions. Although real electronic structures of the npSi with the photophysical properties are still under discussion, the detailed time-resolved studies give some hints to disclose the carrier transition routes. Specifically, indirect bandgap nature is inherited even in nanocrystals smaller than 1.5 nm. Therefore, the carrier transition is very slow causing long lifetime of emission. In contrast, the npSi without diamond cubic lattice can provide short lifetimes such as 1 ns or less as well as organic dyes. Possible mechanisms of light emissions at every wavelength have been summarized to ascertain the future challenges toward industrial use of silicon-based light emitters.

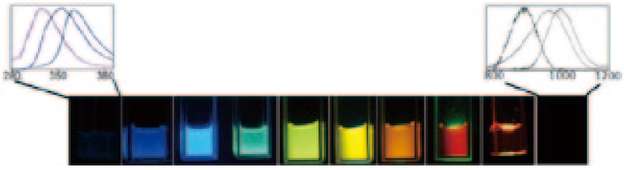

Fig. 1. Continuous tuning in the range between 300 nm and 1000 nm by the fine-structural control over silicon nanoparticles.

*(2) White light emitting Ge nanoparticles.*2)

This paper describes an efficient chemical route for the synthesis of visible light emitting nanocrystals of germanium (ncGe). The synthesis started by heating Ge(II) iodide at 300ºC in argon atmosphere. Spectroscopic characterizations confirmed the formation of diamond cubic lattice structures of ncGe. By grafting hydrophobic chains on the ncGe surface, the dispersions in nonpolar solvents of the ncGe became very stable. The cGe showed the white photoluminescence (PL) feature as shown in Fig. 2. The excitation spectroscopic study concluded that the broad white PL spectrum was described as ensemble of different emission spectral lines. Therefore, the extraction of the specific nanocrystals with predefined emission property allowed for the tuning the color of white PL spectrum. In other words, the color-tuning of white light emission is demonstrated through the witting removal of extra ncGe with unfavorable emission feature by making full use of column chromatographic techniques.

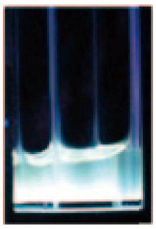

Fig. 2. White light emitting ncSi. White PL spectrum is produced by ensemble of the ncGe emitting the light at different wavelengths.

*(3) NIR emitting Germanium nanocrystals.*3)

We developed a reductant-free facile synthesis process to synthesize germanium nanocrystals (ncGe) passivated with organic monolayers. In this study, the important ability of the primary amine as a reducing agent is demonstrated by comparison it with that of tertiary amine. Interestingly, the significant difference in surface moiety and primal structural phase of the ncGe was caused by the difference in molecular structure of amines, that is, oleylamine and trioctylamine. Due to the trans-configuration of molecular chain and primary amine, oleylamine was much more effective in reducing Ge (II) to Ge (0), and also in protecting surface of the resultant ncGe from surrounding oxygen. The high reactivity of primary amine led to the ncGe synthesis at lower temperature, while the use of tertiary amine caused higher temperature processing. Due to the steric hindrance of three branches, the ncGe synthesized in trioctylamine are more oxidized than the ncGe synthesized in oleylamine. Both ncGe showed room temperature NIR PL feature with the emission maximum at 1275 nm. The spectral line width of the NIR light emission was very narrow, and independent of the molecular structure of amines.

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Toward the Development of Future Materials for Fuel Cells

MANA Independent Scientist Satoshi TOMINAKA

1. Outline of Research

Fuel cells are one of the important power sources for reducing carbon dioxide emissions. For the successful exploitation of them, stable and low-cost electrode materials having catalyst activity and large specific surface area, and electron conductivity are necessary. As such materials, nanostructured precious metals and carbons have been investigated, but those still have issues to be solved for practical applications. Since metal nanostructures have intrinsic limitation on stability because of their relatively weak interatomic bonding, I began to search for new systems which do not have such limitation. I began to search for alternatives in oxides and metal–organic hybrid materials. Here I introduce my recent research works on nano-oxides and hybrid materials.

2. Research Activities

(1) Atomic structure and electronic structure analyses on nanostructured TiO_x.

Reduced titanium oxides are chemically stable and some of them are known to be highly electron conductive, and thus have been expected to be applicable as corrosion-resistant electrodes, which are alternative to precious metals. Recently, we succeeded in the synthesis of nanostructured TiO_x through topotactic reaction, which enabled reduction of TiO_2 nanoparticles without particle growth.[1-3] Interestingly, the reduced phase thus obtained exhibited metallic conduction,[2,3] but the mechanism was not clarified yet.

Thus, the atomic structures of the TiO_x nanomaterials were probed using X-ray pair distribution functions (PDFs, Fig. 1), and the electronic properties were examined using hard X-ray photoelectron spectroscopy (HX-PES) and electron energy loss spectroscopy (EELS).[4] Consequently, we found that the topotactically synthesized phase (*i.e.*, corundum Ti_2O_3) had unique electronic structure, which was attributable to lattice strains. The findings confirm that topotactic reactions can create nanomaterials having unique structures and properties that cannot be realized in bulk materials.

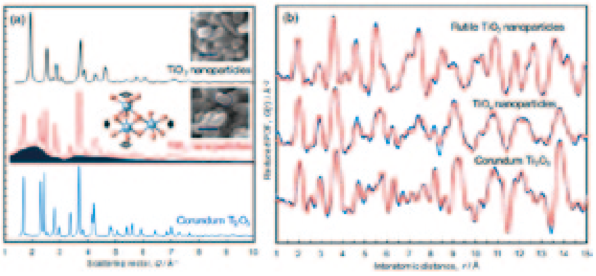

Fig. 1. Atomic structure analyses on TiO_x nanoparticles using X-ray PDFs. (a) X-ray total scattering patterns. The inset scanning electron microscope images show that the morphology was retained during the reduction treatment (scale bar: 30 nm). (b) X-ray PDFs. The experimental plots (blue) were fitted with calculated plots (red).

In addition to that, PDFs clarified presence of an additional phase (most likely Ti_4O_7), which could not be detected by using conventional diffraction measurements. Syntheses of nanomaterials are, generally, more or less kinetically controlled, thus careful analyses, with the presence of additional nanocrystalline or amorphous phases in mind, are needed for the discussion of their properties.[4]

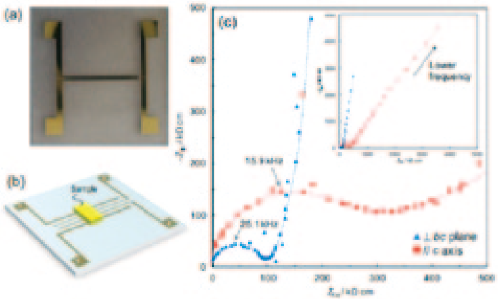

Fig. 2. Single crystal AC impedance measurements. (a) Picture of the Au microelectrodes on a SiO_2 substrate (1 cm × 1 cm, 0.5 mm thick). (b) Schematic for illustrating the overall design. The gaps between electrodes are 20 µm. (c) AC impedance data of a potassium trithiocyanurate crystal.

(2) Metal–organic hybrid materials: synthesis and single crystal analyses.[5]

Metal–organic hybrid frameworks (MOFs) are widely investigated as promising porous materials for gas absorption applications. A variety of structures were synthesized and their properties for gas absorption applications were investigated, while their electronic properties have not been investigated well. In this view, we have synthesized non-porous MOFs, which are analogous with classical inorganic materials, having new structures and investigated their conductivities using microelectrodes designed for measuring single crystal properties.

In order to develop an understanding of the relationship between their crystal structures and conductivities, we used single crystal samples for both the structure analysis and the impedance measurements. Since the influence of grain boundaries is significant in solid-state ion conductors and has to be dealt with carefully, we developed a new setup for single-crystal AC impedance measurements (Fig. 2) in order to understand ion conduction in our crystals. Some of them exhibited proton conductivity under atmospheric conditions. Further works are being carried out to obtain electron conductive materials, and then nanomaterials will be synthesized.

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

MANA Independent Scientist   Katsunori WAKABAYASHI

1. Outline of Research

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

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

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

2. Research Activities

(1) Development of Analytic Method.[1,2]

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

(2) Boltzmann theory of graphene double-layer systems.[3]

Recent progress in graphene research stimulated the fabrication of new functional electronic devices which are composed of graphene and atomically-thin materials. One such system is a graphene double layer structure (GDLS), where two graphene layers are separated by a thin dielectrics (schematically shown in Fig. 1). The GDLS is considered to be a good platform for studying excitonic superfluidity and Coulomb drag effect. An optical device using this system was also proposed as an application. However, theoretical study of the device performance of the GDLS has not been performed sufficiently.

We evaluated the charged-impurity limited carrier mobility in GDLS on the basis of the Boltzmann transport theory, where static screening of Coulomb interaction is treated within random phase approximation. It is found that the carrier mobility strongly depends on the dielectric constant of the barrier layer if the interlayer distance becomes larger than the inverse of the Fermi wave vector. We also show that the carrier mobility as function of an interlayer distance and inner dielectric constants. Our results suggest effective use of ultra-thin dielectric barriers and a practical design strategy to improve the charged-impurity-limited mobility of the GDLS.

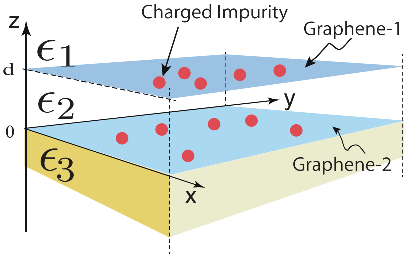

Fig. 1. Schematic of graphene double layer structure with three dielectrics.

(3) Collaboration with experimental group.

Our group is actively performing the collaboration research with several experimental groups internally and externally. We have succeeded to elucidate the carrier scattering mechanism of MoS_2 devices by analyzing the MoS_2 thickness dependence of electric conductivity on the basis of Boltzmann transport theory.[4] Currently, we are also analyzing the Raman spectroscopy measurements of transition metal dichalcogenides using the density functional theory.

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Tailored Synthesis of Nanoporous Metal Particles with Various Architectures

MANA Independent Scientist Yusuke YAMAUCHI

1. Outline of Research

Because of their scientific and practical significance, research on mesoporous materials, conducted mainly by using surfactant assemblies as templates, has been increasing rapidly. The specific features of regular pore arrangement, uniform mesopore size, and high surface area make these materials very promising for various applications.[1-7] Mesoporous metal particles have attracted much attention for years because of their beneficial uses as catalysts. The porous particles provide high surface area and a large number of edges and corners, which are important factors for catalytic applications. In spite of the recent advancements in synthesizing porous nanoparticles, complex and multistep procedures and/or high temperature and pressure conditions are required for the preparation of nanoporous metals. Hence, we focused on designing a straightforward solution phase approach for the high yield synthesis of nanoporous particles with uniform size and morphology. All the nanoporous structures can be simply synthesized by purposefully changing the synthetic parameters including precursor composition (e.g. type and concentration of metal salts and surfactants, and pH) and synthetic conditions (e.g. synthetic temperature and ultrasonic irradiation). The rational design of highly ordered mesoporous metals with controlled compositions and morphologies for practical applications is a most attractive and challenging objective.

2. Research Activities

In a hard-templating method, nanoporous silica with a robust framework is used as a template to synthesize a metal replica. Various Pt nanostructures, such as 1D nanowires and 3D nanowire networks, have been prepared using different templates. Despite those recent advances in the hard-templating method, however, the obtained morphologies have been limited to only powders with irregular morphology or films on conductive substrates. Lack of controllability of the particle sizes and morphological shapes is a serious problem for further development of nanoporous metals. To bring out shape- and size-dependent physicochemical properties, we developed sophisticated hard-templating method to prepare uniform-sized particles with the same shapes in high yield. Lyotropic liquid crystals made of highly concentrated surfactants or block copolymers have been utilized as a soft template. By using chemical or electrochemical reduction, ordered nanoporous metal powders or films can be, respectively, synthesized. However, the ordered arrangement of the rod-self assemblies in the liquid crystals is often distorted during the metal deposition process, resulting in the lack of a long-range order of nanoporous structures in the final product. Recently, we proposed new approach with low-concentrated surfactant solutions. This is a highly reproducible soft-templating method, which is widely applicable to other metal systems.

Very recently, we reported a general "all-wet electrochemical approach" to synthesize novel self-supported 1D Pt nanorods (NRs) with a high density of mesopores (which are denoted as"mesoporous Pt nanorods, MPNRs") by using the assembly of micelles in the confined space of a polycarbonate (PC) membrane. The MPNRs with various aspect ratios can be synthesized by simply controlling the electrodeposition times. The fabrication procedure of 1D MPNRs is schematically illustrated in Fig. 1. The mesoporous structures with a 6–8 nm pore size and a thin wall thickness were well-developed all over the rod surface and inside Pt NRs. The 1D motifs exhibited high activity and CO-tolerant performance in the methanol electro-oxidation (MOR), and our MPNRs showed only 31% loss of ESCA even after a harsh accelerated durability test. Thus, the self-supported mesoporous structures are highly desired in high activity and stability for the large surface area with less aggregation and ripening of Pt nanoparticles. The 1D geometry can maintain improved electron transport characteristics because of the path-directing effects of the structural anisotropy. Also, the mesoporous structures with connected thin walls can provide facile pathways for electron and mass transfer by reducing the interface resistance.

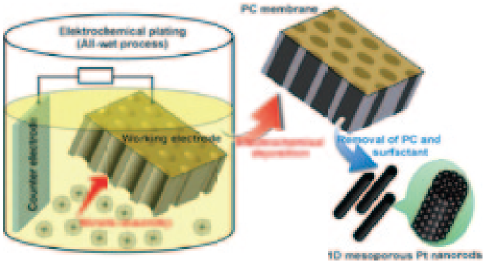

Fig. 1. Electrochemical assembly of micelles in confined space for the preparation of 1D mesoporous Pt nanowires (MPNRs).

This work demonstrates that the selfsupported, 1D, and mesoporous structures are indeed promising architectures to highly improve the catalytic activity and durability of catalysts for the MOR. Such geometrically favorable factors will provide a new avenue in designing highly efficient electrocatalysts used in artificial energy conversion systems.

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Development of MSS-Type Nanomechanical Sensors as a Practical Sensing Platform

MANA Independent Scientist Genki YOSHIKAWA

1. Outline of Research

The demands for new sensors to detect or identify target molecules are rapidly growing in various fields; medicine, security, and environment. Nanomechanical sensors have potential to contribute to these global demands owing to their intrinsic versatility. Based on the newly developed platform "Membrane-type Surface stress Sensor (MSS)," we are now trying to realize useful nanomechanical sensors which can fulfill the practical requirements, such as portability, low-cost, ease of use, in addition to the basic specifications, *e.g.,* high sensitivity that is comparable or better than a typical optical read-out cantilever-type nanomechanical sensors.[1,2]

2. Research Activities

(1) Hand-operated coating & measurements with a USB-powered/operated MSS system.

Recently, we reported a practical approach for coating receptor layers[3] on an MSS chip, that is, a "double-side coating" instead of a commonly used "single-side coating", which requires specific methods or protocols, such as inkjet spotting or gold–thiol chemistry. We demonstrated highly consistent signals even with a simple hand-operated coating as shown in Fig. 1.[4] This "double-side coating" approach is critically important in the case of functionalizing a sensor chip with self-assembled monolayers (*e.g.* silanes or phosphonic acids), which need rather longer (*e.g.* an hour to overnight) incubation in a solution to obtain high quality layers.

As for the measurement system, the latest version of the MSS setup can be operated all by USB-connected/powered devices (Fig. 1). This setup provides an opportunity for anybody to start nanomechanical sensing with high sensitivity and stability, including the coating of MSS chips by *e.g.* hand-operated coating.

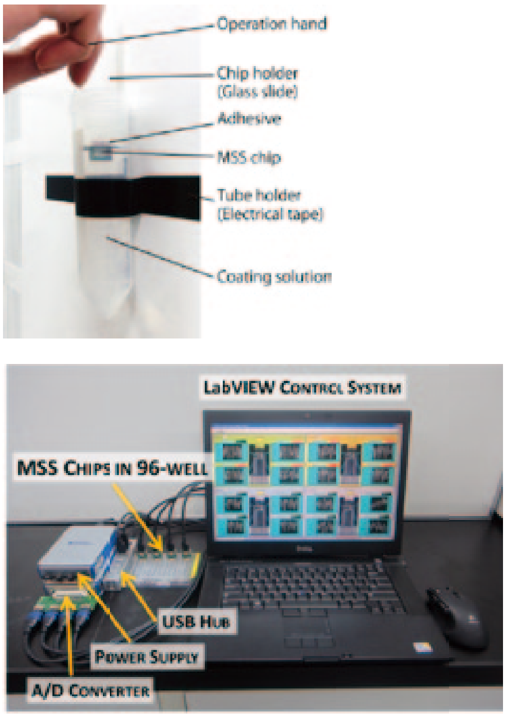

Fig. 1. (Left) Photograph of the hand-operated dip coating setup for creating double-sided coatings for the MSS chip. (Bottom) Photograph of a USB-powered/operated setup compatible with a standard 96-well plate for an entire procedure from coating to measurement.

(2) Demonstration of Breath Analysis for Cancer Diagnosis[5] *— in collaboration with EPFL and University of Basel*

An MSS chip was functionalized with various polymers which react differently to gas samples. The unique signatures from each channel can be used to differentiate complex mixtures of gases and molecules by means of principal component analysis (PCA). Breath samples of both healthy people and patients suffering from a head and neck cancer were analyzed in a double blind trial. The results show a good discrimination between the breath samples of healthy persons and the ones of patients suffering from a head and neck cancer (Fig. 2). This result demonstrates the high potential of MSS for medical diagnosis through breath analysis.

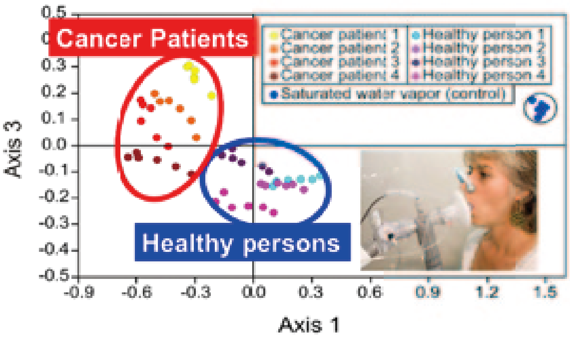

Fig. 2. Principal Component Analysis case scores for breath samples of 4 healthy persons and 4 cancer patients. Each sample has been measured 6 times (colored dots). A breath sample bag containing saturated water vapor has been measured as a control (blue dots). Healthy persons can be clearly distinguished from cancer patients.[5]

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Tuning Electronic Properties of Atomically Thin Nanomaterials: Theoretical Perspective

ICYS-MANA Researcher Sudipta DUTTA

1. Outline of Research

Nanomaterials with atomic thickness show high mechanical stability and provide huge flexibilities of tuning their electronic properties. Our goal is to develop new methodologies based on this class of materials to expedite the realization of futuristic electronic devices with deep theoretical understanding of underlying mechanisms. That necessitates a multifaceted theoretical investigation of the limitations in real systems, such as domain formation, defects, impurities, substrate effects etc. We further plan to tune their electronic properties by means of doping, structural and chemical modifications with a thorough investigation of the correlation effects and by admixing different functionalities in their hybrid superlattice structures in search of advanced functionalities. We adopt tight-binding and density functional level of theory along with many-body configuration interaction (CI) numerical method for theoretical explorations.

2. Research Activities

(1) Domain Formation in Graphene.

Because of the existence of multiple growth nuclei during chemical vapor deposition (CVD), the several domains meet each other with different crystallographic angles, forming the domain walls. They can act as scattering centers and significantly modify the electronic structure. To create the experimental environment of CVD experiment, we let the separate graphene flakes to interact with each other at their surface. The optimized geometries show the formations of smooth crystallographic geometry along with stable defective grain boundaries comprising of different sized carbon rings. We further explore the effect of domain walls on the transport properties of graphene.

(2) Thin layer Fullerene as Substrate.

The performance of graphene devices largely depends on the substrates. The substrate should be chosen in such a way that, it can not alter the inherent properties of devices. We choose thin layer of fullerene as a substrate. Owing to their spherical shape, fullerene minimizes the contact area with top layer graphene. As a result, the linear dispersion of graphene at Dirac point remains unchanged.

(3) Effect of Electronic Correlation.

The reduced electronic degrees of freedom in atomic-sheets make the consideration of electronic correlation effects inevitable for theoretical investigations of certain properties like magnetic and transport. We investigate the ribbon structures of honeycomb lattice with zigzag edges using CI method on the basis of Hubbard Hamiltonian. For the half-filled case, the ground state shows gapless spin excitations over the flat band region,[1] a characteristic feature of zigzag graphene ribbons. The charge gap shows minima at Dirac point, which is consistent with the mean-filed results. Increase in electronic correlation results in increased charge gap and reduced spin gap. Hole doping reduces the spin and charge gap, making the ground state conducting and magnetic. We further investigate the effect of scattering processes considering finite quantum dot structures and arrived at similar observations.[1]

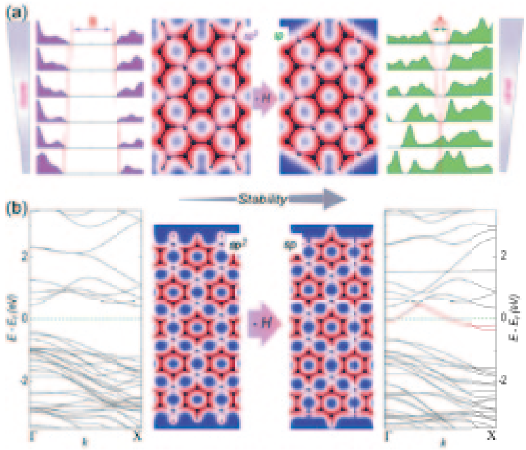

Fig. 1. (a) The density of states with increase in width of armchair BC_3 ribbons with (left) and without (right) passivating hydrogen on edge boron atoms. (b) The band structures of zigzag BC_3 ribbons with (left) and without (right) passivating hydrogen on edge boron.

(4) Beyond Graphene: Monolayer BC_3.

We have been continuing the exploration of other two-dimensional materials like BC_3. Unlike graphene, it exhibits semiconducting behavior arising from Kekulé-like charge localization with aromatic carbon hexagons, separated by anti-aromatic hexagons consisting of carbon and boron atoms. We study the quasi one-dimensional ribbon structures of BC_3 with both armchair and zigzag edges mainly highlighting the effect of hydrogen passivation of edges. We observe that, the removal of passivating hydrogen from the edge boron atoms makes them sp-hybridized, increasing their stability by enhanced aromaticity. The semiconducting ribbons become metallic upon removal of passivating hydrogen from edge borons (Fig. 1a). With increase in armchair ribbon width, the bulk semiconducting property prevails, giving rise to an anomalous behavior of gap opening.[2] In case of zigzag ribbons, the appearance of robust edge states at Fermi energy results in metallicity (Fig. 1b) which does not change upon increase in width.[3]

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Reversible and Instantaneous Swelling of Inorganic Layered Materials

ICYS-MANA Researcher **Fengxia GENG**

1. Outline of Research

Inorganic materials with layered structures possess strong structural anisotropy with covalent bonding in the layers while weaker layer-to-layer interactions such as van der Waals' force or electrostatic attractions, which endows the materials with the capacity of incorporating ions and/or solvent species into the interlayer region, resulting in layer-to-layer gallery expansion or swelling. However, the swelling is either limited to a few nanometers or sometimes macroscopic but accompanied with partial or complete exfoliation into unilamellar sheet units, i.e., nanosheets, which are receiving burst of research interest due to their superior properties compared with their three-dimensional counterparts. Despite of continuous efforts on exfoliating various layered materials, such as the well-known graphite, layered metal dichalcogenides, layered double hydroxides, and some oxides,1) study on the extremely highly swollen structure, which is of paramount importance to understanding the exfoliation process and the resultant two-dimensional nanosheets, remains a great challenge given the low structural stabilities of extensively swollen phases. Therefore we tried to wisely select the electrolyte that is utilized in the swelling process to obtain an extensively swollen phase, which provides essential basis for both deep understanding of the swelling mechanism and controlled exfoliations.

2. Research Activities

We took a typical layered material, $H_{0.8}[Ti_{1.2}Fe_{0.8}]O_4 \cdot H_2O$ for illustration study. The structure consists of stacking of $[Ti_{0.6}Fe_{0.4}]O_2^{0.4-}$ layers with a spacing of 0.89 nm. While base of a bulky symmetric ion, tetrabutylammonium hydroxide (TBAOH, $(C_4H_9)_4NOH$), was usually adopted for exfoliation purposes, a polar amine, dimethylaminoethanol (DMAE, $(CH_3)_2NC_2H_4OH$), was selected for present study.2) After dispersing the crystals in DMAE solutions, sample volume increase was observed immediately. Fig. 1a schematically illustrates the swollen structure, with swelling solely along the layer stacking direction. The layer distances expand from original 0.89 nm to 90 nm at the maximum, i.e. 100-fold swelling. The optical microscope characterizations showed that the swollen crystals exhibit uniform color along one crystallite, suggesting the crystal swelling is homogeneous.

The swelling occurs rapidly, finishing in just a few seconds. Fig. 2 shows real-time images. After dropping DMAE solution, the volume increase occurred immediately and the crystals swelled beyond 200 μm in 1.4 s. This process is reversible. With addition of HCl, the crystals can shrink back to the original sizes also in a split second. In both swelling and shrinking, the crystals behave as a unit without any sign of thinning or exfoliations, which is much different from easy observations of crystal falling apart when using TBAOH as the electrolyte.

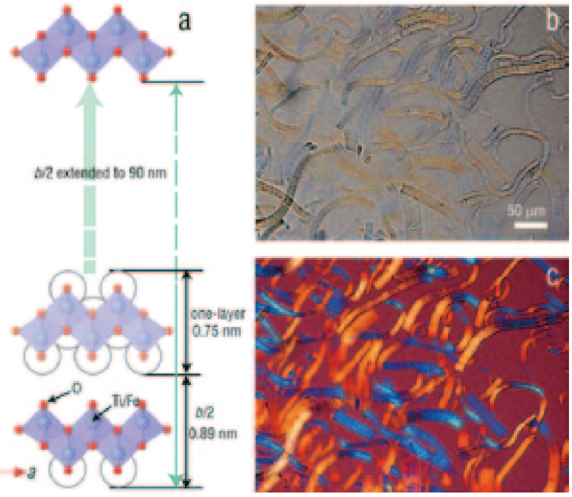

Fig. 1. (a) Schematic illustration of the swollen structure. (b) An optical microscope image at the maximum swelling. (c) The optical microscope image taken with cross polarizer.

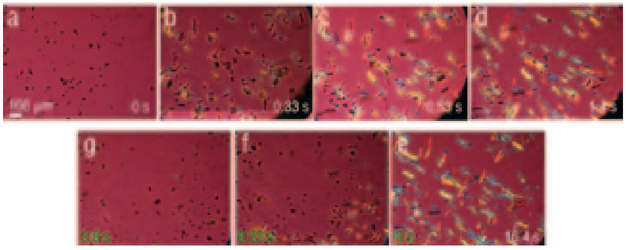

Fig. 2. Time-series images of the $H_{0.8}[Ti_{1.2}Fe_{0.8}]O_4 \cdot H_2O$ crystals in the swelling and shrinking process. (a) The starting material. (b-e) Images collected at 0.33, 0.53, 1.4, and 16.4 s after one drop of DMAE addition, (f-g) 0.53 and 3.8 s after HCl addition.

Through first-principle calculations on the radial distribution functions of H_2O from the DMAE or TBAOH molecules, it was found that the water molecules around DMAE tend to direct themselves differently at the nitrogen end and oxygen end, whereas such directional ordering is absent in TBAOH case (Fig. 3). The long-range H_2O structuring helps to stabilize the highly swollen structure.

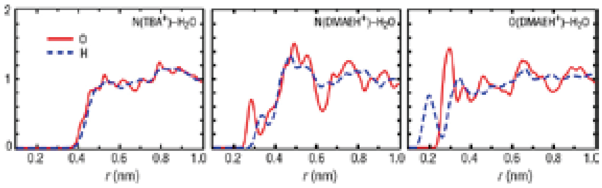

Fig. 3. The radial distribution functions *g(r)* of water from N in TBAOH (left panel), N in DMAE (middle panel), and O (-OH) in DMAE.

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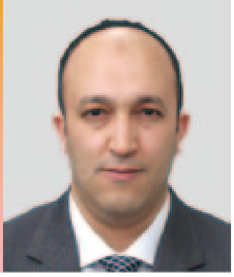
Self-Assembled Monolayers Toward New Dynamic and Magnetoresistive RAM

ICYS-MANA Researcher Hicham HAMOUDI



1. Outline of Research

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

2. Research Activities

(1) Building block strategy.

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

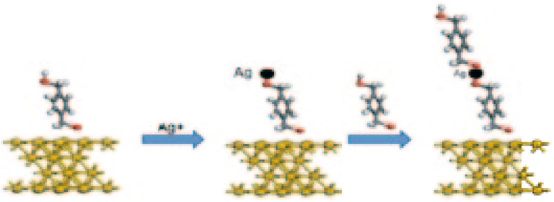


Fig. 1. Scheme to prepare BDMT-Ag-BDMT system.

(2) Freestanding Organometallic Nanosheets.

Using the bottom-up approach (Fig. 1) I have built a new generation of materials considered as surfaces without bulk “freestanding organometallic nanosheets”[3)] with a nanometer thickness for the mono- and multi- layer sheets, and a lateral dimension in the millimeter range from crosslinked aromatic (BPD- M) self-assembled monolayer. After cross-linking of the (BPD-M) SAMs, the freestanding organometallic nanomembranes have been released by the dissolving of the underlying substrate or by scission of the anchor group-substrate bonds. Fig. 2 shows freestanding Carbon-metal nanosheets, which is one of the derivative products of the freestanding organometallic nanosheets.

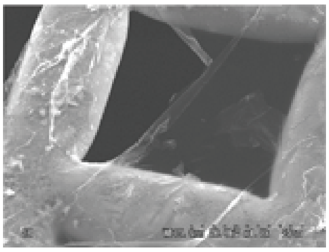


Fig. 2. Freestanding Carbon-metal nanosheets, with thickness of 3 nm.

(3) Molecular electronics.

Various studies indicate the significant role played by the class of molecular system consisting of organometallic redox-active centers. The implementation of this type of architecture will open up new vistas for a new class of materials for transport, storage, and computing. In this context, a bottom-up approach is provided to build a crossbar device using the crosslinked Self-assembled monolayer of the (BPD- Ni^{+2}) on gold surface (Fig. 3).[4)]

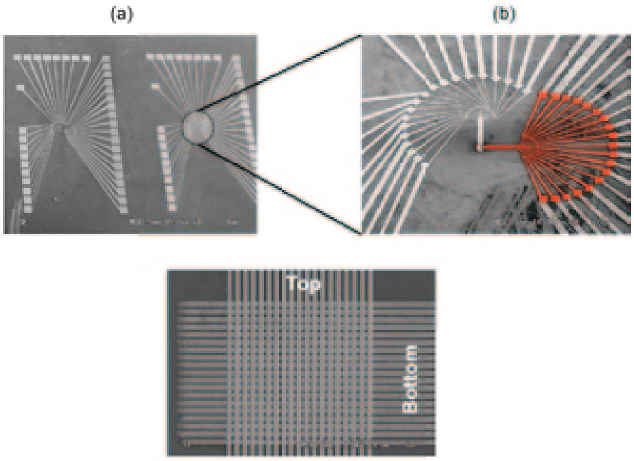


Fig. 3. SEM images of the crossbar devices.

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Supramolecular Nanomaterials with Dynamic and Sensing Functions

ICYS-MANA Researcher Shinsuke ISHIHARA

1. Outline of Research

Materials emerge to demonstrate interesting functions when they are nano-structured, assembled, and organized. The purpose of my research is to design and synthesize of functional nanomaterials based on such ‘supramolecular concept’, which will be useful for energy, environmental, and nanotechnological applications. My materials involve layered double hydroxides,[1–4] porphyrins,[4–7] porous materials,[8–10] and liquid crystals.[11] Representative accomplishments are introduced blow.

2. Research Activities

(1) Dynamic Breathing of CO_2 by Hydrotalcite.[1]

The carbon cycle of carbonate solids (e.g., limestone) involves weathering and metamorphic events, which usually occur over millions of years. Here we show that carbonate anion intercalated layered double hydroxide (LDH), a class of hydrotalcite, undergoes an ultrarapid carbon cycle with uptake of atmospheric CO_2 under ambient conditions (Fig. 1). The use of ^{13}C-labeling enabled monitoring by IR spectroscopy of the dynamic exchange between initially intercalated ^{13}C-labeled carbonate anions and carbonate anions derived from atmospheric CO_2. Exchange is promoted by conditions of low humidity with a half-life of exchange of ~24 h. Since hydrotalcite-like clay minerals exist in Nature, our finding implies that the global carbon cycle involving exchange between lithosphere and atmosphere is much more dynamic than previously thought.

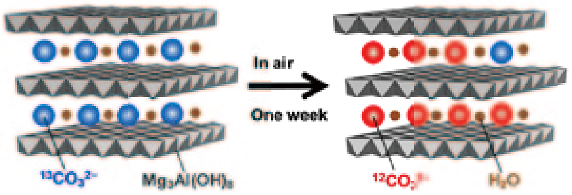

Fig. 1. Dynamic exchange of carbonate anions of LDH with atmospheric CO_2.

(2) Methanol Sensor.[4]

Methanol is a highly toxic substance, but it is unfortunately very difficult to differentiate from other alcohols (especially ethanol) without performing chemical analyses. We report that a composite film prepared from oxoporphyrinogen (OxP) and a layered double hydroxide (LDH) undergoes a visible color change (from magenta to purple) when exposed to methanol, a change that does not occur upon exposure to ethanol (Fig. 2). Interestingly, methanol-induced color variation of the OxP-LDH composite film is retained even after removal of methanol under reduced pressure, a condition that does not occur in the case of conventional solvatochromic dyes. The original state of the OxP-LDH composite film could be recovered by rinsing it with tetrahydrofuran (THF), enabling repeated usage of the composite film.

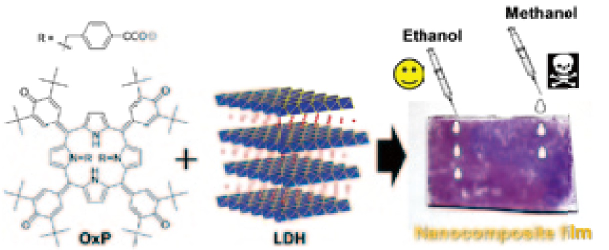

Fig. 2. Naked-eye discrimination of methanol from ethanol using composite film of oxoporphyrinogen and layered double hydroxide.

(3) Clay-actuator.[3]

A particular type of LDH can homogeneously incorporate differently-sized alcohols at its interlayer space to form a self-assembled mono- or bi-layer. Unlike conventional ion-exchange-driven intercalation in clays, intercalated alcohol molecules are bound to the water contained in the LDH crystalline layers through weak hydrogen bonds permitting smooth molecular interdiffusion. This latter process ensures homogeneity of the self-assembly layer within LDH even if differently-sized alcohols are intercalated. Surprisingly, synchrotron-XRD proved that the interlayer distance of the LDH can be controlled with sub-Ångström precision by altering the mole ratio of the intercalated alcohols.

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Polymeric Nanomaterials for Biomedical Application

ICYS-MANA Researcher **Yohei KOTSUCHIBASHI**

1. Outline of Research

It is of great interesting that polymeric materials show different physicochemical properties by their structures such as linear polymers, branched polymers, cyclic polymers, surface modifications, and gels even though they are made from exactly same monomers.[1-4] Over the last decade, design of these polymeric materials (*e.g.* molecular weight, composition, structure, functionality, and conjugation) has become simple with development of synthetic techniques of controlled/living radical polymerizations (CLRPs) and click chemistry. Using a combination of these techniques, polymeric nanomaterials were created for biomedical applications.

2. Research Activities

(1) Dual-temperature and pH responsive (ethylene glycol)-based nanogels.[5]

Nanogels are cross-linked structures formed by covalent bonds, hydrophobic interaction, electrostatic interaction, and coordinate bond, and they have been used as carriers due to their high stability, high drug loading capacity, and for their ability to incorporate various materials such as peptides, proteins, nucleic acids, and inorganic particles. It is a challenge to add multi-stimuli responsive properties to a gel for biomedical applications. We achieved to prepare a dual-temperature and pH responsive (ethylene glycol)-based nanogels by CLRPs in aqueous solution at 37°C having different sizes and compositions without use of surfactant (Fig. 1). The calculated weight-percent of ethylene glycol units in the gels were over 60 wt% and these high ethylene glycol contents are expected to lead high biocompatibilities to the nanogels.

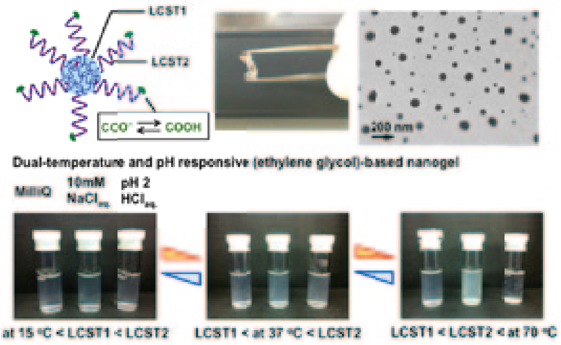


Fig. 1. Dual-temperature and pH responsive (ethylene glycol)- based nanogels.

(2) Simple coating with polymer functionalized silica nanoparticles for controlled surface properties.[6]

Water-repellent surfaces are importance for a range of applications such as self-cleaning, anti-frost surface, water corrosion-resistance, and effective solution transport and its practical use will give economic benefits to our daily life. These surfaces are usually achieved by hydrophobic property and high roughness structures. We found a mixture of polymer-silica nanoparticles (P-SiNPs) having different sizes to change the surface properties of substrates remarkably as compared to one containing P-SiNPs having uniform-sizes. High surface roughness was constructed by the mixed P-SiNPs as very little coating materials, which is beneficial from an economical point of view. This inexpensive system provides a simple, quick, and effective approach to changing the surface properties of substrates that could be exploited for large-scale surface modification (Fig. 2).

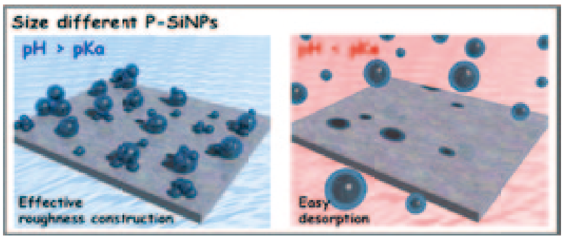
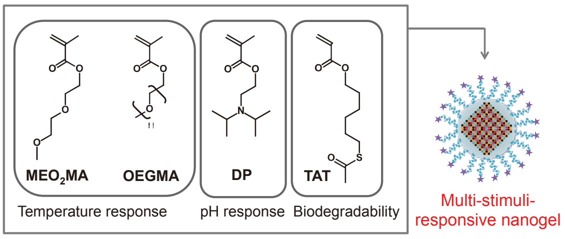


Fig. 2. Size different P-SiNPs for controlled surface properties of substrates by simple coating methods.

(3) Multi-stimuli-responsive nanogels consisting of four types of monomers.

Living body is performing excellent metabolism with building/collapsing, and polymeric materials have to avoid/utilize the living system to achieve their aim. Usually, polymeric nanomaterials work as drug carriers have to possess four abilities *i.e.* biocompatibility, interaction with target cell, escape from lysosome, and biodegradability. To add the abilities, nanogels consisting of four types of monomers were successfully prepared by CLRPs (Fig. 3).



MEO_2MA: Di(ethylene glycol)methyl ether methacrylate, **OEGMA:** Oligo(ethylene glycol)methyl ether methacrylate, **DP:** 2-(Diisopropylamino)ethyl methacrylate, **ATA:** 6-acetylthiohexyl acrylate

Fig. 3. Multi-stimuli-responsive nanogels having dual-temperature responsive, pH responsive, and biodegradable properties.

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Two-Dimensional Materials for Ultimate Electronics

ICYS-MANA Researcher **Song-Lin LI**

1. Outline of Research

The miniaturization of electronic devices has been the principal driving force behind the semiconductor industry, which has brought steady improvements in computational ability and device cost. However, the prevailing silicon electronic technology will approach its physical limit around 2025 due to the short-channel effect and the inherent channel roughness. To overcome these limitations for further miniaturization, new materials with atomic thinness and flatness will be required in near future.

Although numerous nano and molecular materials have been proposed as the post-silicon channel materials, such as one-dimensional (1D) carbon nanotubes, molecules and graphene, none is proven to be technologically viable. For example, the carbon nanotubes require strict controls on chirality and alignment, which remain a big challenge to meet the industrial level; the issue of graphene is the lack of intrinsic energy gap. Recently, 2D metal chalcogenides emerged as promising candidates due to exceptional integration of requirements for the post-silicon channels, such as presence of atomic thickness and flatness, process compatibility and sizable energy gap. Such merits lay the foundation in realizing technologically viable atomic transistors, which represent the ultimate microelectronic technology. Before practical use, several physical and technological issues have to be addressed. In this study, the carrier injection and scattering mechanisms in MoS_2 atomic layers are investigated.

2. Research Activities

(1) Carrier Injection into 2D semiconductors.

Understanding charge injection at electrode/channel interfaces, i.e., electrical contact, is fundamental in realizing high-performance devices. Such an issue is particularly important for devices made from low-dimensional semiconductors where quantum and surface effects emerge.

Here, we develop a sticky exfoliation method to obtain super-consecutive MoS_2 atomic layers, which enable us to systematically investigate the evolution of interface property between metal electrodes and 2D semiconductors as semiconductor thickness (t) shrinks. Remarkably, we observe the quantum confinement effect on Schottky barrier at Au/MoS_2 interface. The contact resistivity (ρ_c) exhibits a monotonic dependence on t: it decreases with reducing t in samples >5 layers, while it increases with further reducing t (Fig. 1a). The trend of ρ_c increase in extremely thin samples is line with that of energy gap expansion due to quantum confinement effect. The carrier injection is dominated by a thermal field emission mechanism. The interfacial Schottky barrier is estimated to increase from 0.3 to 0.5 eV as MoS_2 shrinks from 5 to 2 layers. An expansion asymmetry in energy levels is also observed. The upshift of conduction band is smaller than the downshift of valence band in the n-type MoS_2. These findings add new knowledge into low-dimensional physics.

(2) Carrier Scattering Mechanism.

A long-standing puzzle in 2D semiconductors is the low carrier mobility (μ) as compared with corresponding bulk structures, which constitutes the main hurdle for realizing high-performance devices.

To address this issue, we perform combined experimental and theoretical study on atomically thin MoS_2 field effect transistors with different number of layers (NLs).[1] Experimentally, an intimate μ-NL relation is observed with a 10-fold degradation in μ for extremely thinned monolayer channels. In order to accurately describe the carrier scattering process and to shed light on the origin of the NL-induced mobility degradation, a generalized Coulomb scattering model is developed with strictly considering device configurative conditions, i.e., asymmetric dielectric environments and lopsided carrier distribution. We reveal that the carrier scattering from interfacial Coulomb impurities (e.g., chemical residues, gaseous adsorbates and surface dangling bonds) is greatly intensified (Fig. 1b) in extremely thinned channels, resulting from shortened interaction distance between impurities and carriers. Such a pronounced factor may surpass lattice phonons and serve as dominant scatterers. This understanding offers new insight into the thickness induced scattering intensity, highlights the critical role of surface quality in electrical transport and would lead to rational performance improvement strategies for future atomic electronics.

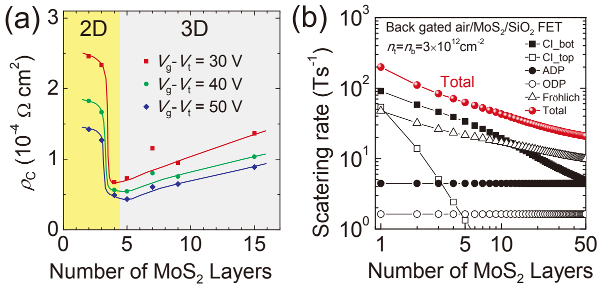

Fig. 1. (a) Contact resistivity (ρ_c) vesus channel thickness. In 3D regime (t > 5 layers), ρ_c decreases with reducing t, while it increases with further reducing t in 2D regime due to quantum confiment effect. (b) Calculated scattering rates for different mechanisms, including Coulom impurity (CI) at bottom (bot) and top surfaces, lattice deformation by acoustic and optical phonons (ADP and ODP), and Fröhlich interaction.

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Double Molecular Switches for Fullerene Complexation and Transport in Different Solvents

ICYS-MANA Researcher Huynh Thien NGO

1. Outline of Research

Though fullerenes are promising materials, their applications have been so far extremely limited due to their low solubility in conventional solvents. Higher solubility can be achieved by using benzene or toluene as solvent although the use of these solvents in real life applications, *e.g.* medicinal science and nanotechnology, is precluded by their high toxicities. Therefore, improvement of the solubility (or availability) of fullerenes, especially in water, has become a hot topic.[1] For solubilization of fullerenes (or other materials), the use of surfactants which undergo van der Waals interactions and/or π-π stacking interactions with fullerenes are particularly interesting since the well dispersed fullerenes will have unchanged intrinsic structure and properties.[2,3] Having that in mind we design tweezer-like surfactant-containing porphyrins with switchable tertiary amine groups, connected by a linker (Fig. 1). The photoresponsive property of the linker allows us to employ light to mediate the capture and release fullerenes while the gas responsive switch unit is responsible for the amphiphilicity and therefore the transport of fullerene between different solvents.[4]

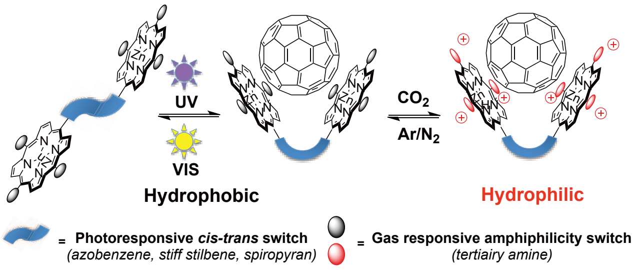

Fig. 1. Photo and gas responsive switch for fullerene capture and transport.

2. Research Activities

(1) Synthesis of individual switches.

To realize an ideal cooperative gas- and photoresponse of the desired system, each of the separate switching unit must function optimally. Therefore, a number of porphyrins containing different individual switching units were prepared in order to investigate their switching ability (Fig. 2). Each of these switches is subjected to an optimization process to determine the best candidate to be combined in one single multi-tasking molecular machine. Due to their different basicity both aliphatic and aromatic dimethyl and diethyl tertiary amines were prepared as gas responsive units. Their response to CO_2 and N_2 gas will be investigated. Azobenzene, stiff stilbene and spiropyran are good candidates as photo responsive linker. Their conformational switching properties under influence of light and/or heat have been studied thoroughly. By linking such large systems as porphyrin, one must determine the power/energy needed to achieve high switching yields and which systems are most efficient for the desired properties.

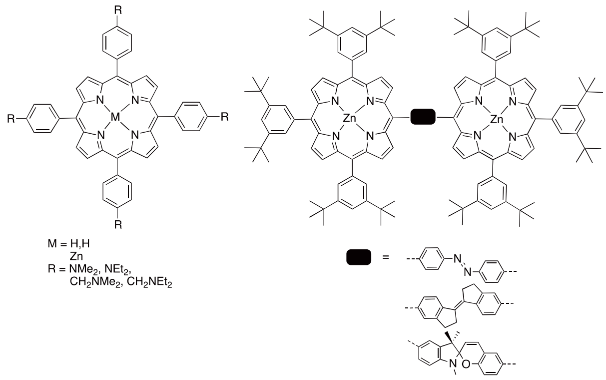

Fig. 2. Porphyrin with individual switching units.

(2) Gas-responsive switching experiment.

The first tests with free-base aliphatic dimethylaminoporphyrin showed clearly the transport of the switch to the water phase occurred within minutes after purging CO_2 through the mixture (Fig. 3). This was observed with both the UV-VIS experiments and the naked eyes. The back transport to the organic phase happened faster once N_2 was purged to the solution although partially protonation of the inner N atoms were observed. Experiments with aliphatic diethylaminoporphyrin containing Zn proved to be more efficient without protonation of the inner N-atoms. Next, aromatic aminoporphyrins will be subjected to similar experiments and the switching ability of the photo responsive linker will be investigated.

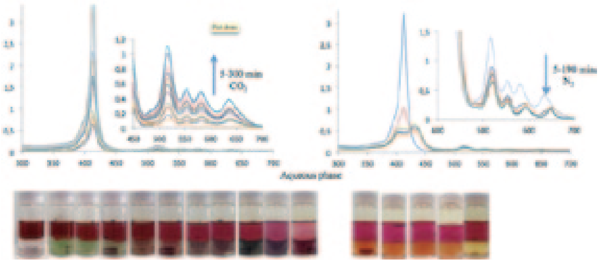

Fig. 3. Gas responsive switching experiments with aliphatic amino porphyrin.

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

ICYS-MANA Researcher Liwen SANG

1. Outline of Research

III-Nitride semiconductor, which includes GaN, AlN, InN and their ternary and quarternary alloys, has the tunable direct bandgaps from the infrared (InN at 0.65 eV) through the visible and the ultra-violet (UV) (GaN at 3.42 eV) to the deep UV region (AlN at 6.2 eV). They also have the advantages of high drift velocity, high radiation resistance, large absorption coefficient, and high carrier mobility. These superior properties provide their promising applications in the high-efficiency photo·electricity energy conversion devices, such as solid-state light emitting diodes (LEDs), high-performance photodiodes and ultra-high efficiency (~50%) solar cells.

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

2. Research Activities

(1) Super-wide spectrum response in solar cells.

The concept of intermediate-band (IB) transitions was first proposed by Luque and Marti in 1997. It consists of an IB material sandwiched between two ordinary *n*- and *p*-type semiconductors, in which the sub-bandgap-energy photons are absorbed through the transitions from the valence band (VB) to the IB and from the IB to the conduction band (CB), adding up to the photovoltaic current. Theoretically, the IB solar cells provide additional tolerance to match the solar spectrum toward a maximum conversion efficiency by modulating the energy level of the IBs. From this perspective, III-Nitride InGaN is the best choice which can provide a high-quality wide-bandgap host material. To fabricate the IB solar cells, we introduced a multiple quantum dots (QDs) stack with high In compositions inside the low-In InGaN p-n junctions (Fig. 1a). The transition through IBs which were formed from QDs was experimentally and theoretically demonstrated. The achievement of the IBs leads to a superwide photovoltaic current response from the UV to near infrared region, covering most of the strong luminescence in the sun light (Fig. 1b). As a result, a significant improvement in the short-circuit current density was achieved. To the best of our knowledge, this is the first experimental demonstration of not only the IB absorption in the III-Nitride material system but also the multiple IBs in the photovoltaic field.

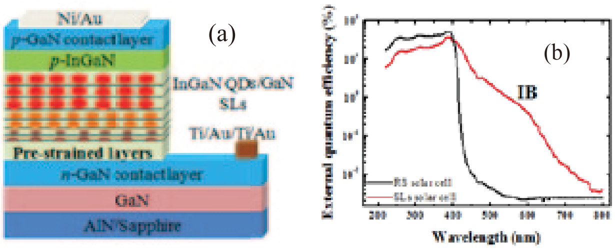

Fig. 1. (a) The schematic structure of the InGaN IB solar cells. (b) External quantum efficiency of the reference solar cell and IB solar cell. The IB solar cell shows a wider spectrum response.

(2) Tunable-wavelength LEDs.

To achieve the high-brightness white light illumination, three primary color integration including red, green and blue light emitting diodes (LEDs) is considered to be the most efficient method. Up to now, green and blue light emitting have been realized by using InGaN/GaN quantum wells with an In composition around 10-20%. AlGaInP is used as the material to generate red light. Therefore, the integration of the three primary colors needs complex bonding process and driving circuit design. If three primary colors can be realized inside one material system, the cost will be greatly reduced. Theoretically, red light can be generated using InGaN-based quantum wells with an In composition around 40%. However, due to the large lattice mismatch, the quality of In-rich InGaN is very poor, which lead to the long-wavelength light emitting impossible. To develop long-wavelength red LED structures, the pre-strained layers InGaN/GaN short-period superlattices were deposited on the *n*-GaN before the active region. The pre-strained layer helped to incorporate more In the active region, and led to the luminescence more than 610 nm (Fig. 2).

Fig. 2. The color image of LED with applied voltage of 4, 6, and 7 V.

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Growth Mechanism and Mechanical Properties of Nanotubes Investigated by *In Situ* TEM

ICYS-MANA Researcher Dai-Ming TANG

1. Outline of Research

Nanotubes, including carbon nanotubes (CNTs) and inorganic nanotubes, have attracted wide-spread research interest because of their unique properties and broad applications. Understanding the growth mechanism at atomic level is of key importance for the controlled synthesis. And direct measurement of the structure-dependent mechanical properties is vital for their applications in nanoelectromechanical systems (NEMS). In our work, *in situ* transmission electron microscopy (TEM) is used to tackle these two major challenges, the growth mechanism and mechanical properties.

2. Research Activities

(1) Structural Changes in Iron Oxide and Gold Catalysts during Nucleation of Carbon Nanotubes.[1)]

We report a simple, versatile *in situ* transmission electron microscopy (TEM) approach for investigating the nucleation and growth mechanism of carbon nanotubes (CNTs), by which the composition, phase transition and physical state of various catalysts can be clearly resolved. In our approach, catalyst nanoparticles (NPs) are placed in a multi-wall CNT "tubular furnace" with two open ends, and a high temperature is obtained by Joule heating in the specimen chamber of a TEM. The carbon is supplied by electron irradiation-induced injection of carbon atoms. Comparative studies on the catalytic behavior of traditional iron oxide and recently discovered gold catalysts were performed. It was found that the growth of CNTs from iron oxide involves the reduction of Fe_2O_3 to Fe_3C, nucleation and growth of CNTs from partially liquefied Fe_3C, and finally the formation of elemental Fe when the growth stops (Fig. 1). In contrast, while changes in shape, size and orientation were also observed for the fluctuating Au NPs, no chemical reactions or phase transitions occurred during the nucleation of CNTs (Fig. 2). These two distinct nucleation and growth processes and mechanisms would be valuable for the structure-controlled growth of CNTs by catalyst design and engineering.

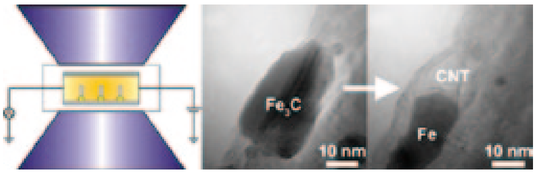

Fig. 1. ***In situ*** **TEM observations of the nucleation and growth of a CNT from an iron oxide catalyst NP. The NP was Fe_3C during the nucleation and transformed into elemental Fe when the growth terminated.**

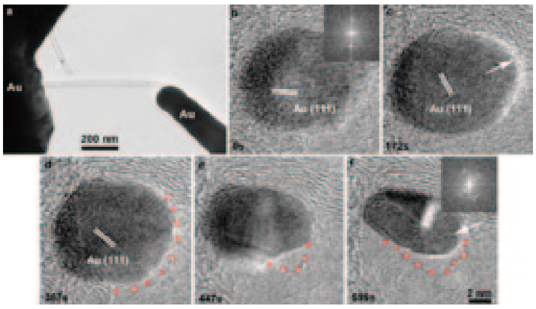

Fig. 2. ***In situ*** **TEM observations of the nucleation of a CNT from an Au catalyst NP. While structural fluctuations were observed during the lifting of the carbon cap, no chemical reactions or phase transitions occurred.**

(2) Anomalous Tensile Properties of WS_2 Nanotubes.[2)]

Mechanical properties and fracture behaviors of multiwalled WS_2 nanotubes produced by large scale fluidized bed method were investigated under uniaxial tension using *in situ* transmission electron microscopy probing; these were directly correlated to the nanotube atomic structures (Fig. 3). The tubes with the average outer diameter ~ 40 nm sustained tensile force of ~2949 nN and revealed fracture strength of ~11.8 GPa. Surprisingly, these rather thick WS_2 nanotubes could bear much higher loadings than the thin WS_2 nanotubes with almost "defect-free" structures studied previously. In addition, the fracture strength of the "thick" nanotubes did not show common size dependent degradation when the tube diameters increased from ~20 nm to ~60 nm. HRTEM characterizations and real time observations revealed that the anomalous tensile properties are related to the inter-shell crosslinking and geometric constraints from the inverted cone-shaped tube cap structures, these resulted in the multishell loading and fracturing.

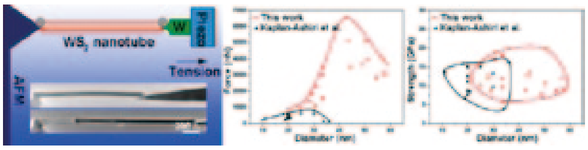

Fig. 3. **Experimental configuration during the** ***in situ*** **TEM tensile tests. Plots of the ultimate tensile force (a) and strength (b) of WS_2 nanotubes against their outer diameter. Our** ***in situ*** **TEM measurement results (red dots) are demonstrated along with the published data by Kaplan-Ashiri et al. (black triangles) obtained by** ***in situ*** **SEM tensile method.**

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Advanced Anode Materials for Lithium-ion Batteries and Their Storage Mechanisms at Atomic Scale

ICYS-MANA Researcher Xi WANG

1. Outline of Research

Lithium-ion batteries (LIBs) can deliver high levels of energy storage density and offer long operating lifetimes,[1-4] but their power density is too low for many important applications. Therefore, we developed some new strategies and fabricated novel electrodes for fast Li transport and its facile synthesis including N-doped graphene-Fe_2O_3 sandwich papers, and Co_3O_4 nanocages. In addition, by using advanced in-TEM techniques and the theoretical simulations, we systematically studied and understood their storage mechanisms at the atomic scale, which shed a new light on the reasons of the ultrafast lithium storage property and high capacity for these advanced anodes.

2. Research Activities

(1) Synthesis of advanced anode materials.

An essential component of the current endeavour in this area is to design advanced candidate anodes for the next generation of LIBs. Among the candidates, Fe_2O_3, spinel Co_3O_4 and N-doped grapheme (GN) have attracted enormous attention because of its several inherent advantages. However, there are still challenges on developing some feasible strategies for making ultrafast electrodes for above candidates. A new facile route to fabricate N-doped graphene-Fe_2O_3 sandwich papers (Fig. 1a) is developed by an introduction of the 7,7,8,8-tetracyanoquinodimethane anion ($TCNQ^-$).[2] If used in lithium-ion batteries (LIBs), the material exhibits a large capacity, high rate capability, and excellent cycling stability. The superior electrochemical performance of this novel material is the result from its unique features: excellent electronic conductivity related to the sandwich structure, short transportation length for both lithium ions and electrons, and elastomeric space to accommodate volume changes upon Li insertion/extraction. In addition, we report the synthesis of unusual single-crystal Co_3O_4 nanocages with highly exposed {110} reactive facets (Fig. 1a)[3] via a one-step solution method. When tested as anode materials in lithium-ion batteries, these Co_3O_4 nanocages deliver a high reversible lithium storage capacity of 864 mAh g^{-1} at 0.2C over 50 cycles and exhibit an excellent rate capability. The dominantly exposed {110} planes, a high density of atomic steps in nanocages, and the large void interiors lead to the regarded superior electrochemical performance.

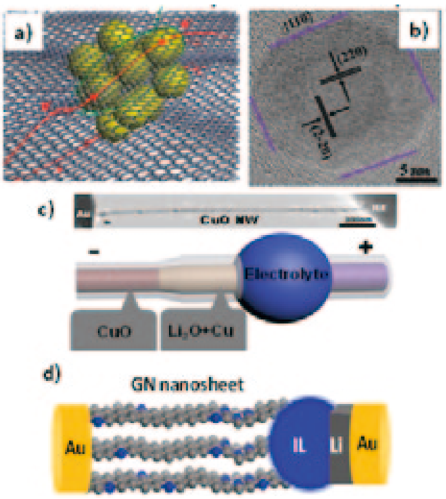

Fig. 1. a) Schematics of as-made N-doped graphene-Fe_2O_3 sanwich papers. b) TEM image of as-made Co_3O_4 nanocage. c) Schematic illustration of an electrochemical device constructed inside the TEM. This consists of a CuO NW anode, a droplet of the ionic liquid electrolyte (ILE), and a Li metal electrode. d) Schematic illustration of the in situ TEM electrochemical experiment setup. A GN nanosheet is glued to an Au rod, and Li metal on the Au probe makes the other electrode.

(2) Nanoscale energy storage mechanisms under TEM.

Up to now, there are few reports on direct experimental evidence and fundamental understanding of the lithium storage mechanisms at the atomic scale. Revealing these for them may shed a light on the reasons of its ultrafast lithium storage feature and high capacity found in the experiments. And there still remain other issues, such as SEI composition, the differences between the material edges and its surface in storing mechanism. by using advanced in-situ TEM, we directly investigated these processes using an individual CuO nanowire anode and constructed a LIB prototype within a TEM (Fig. 1c).[4] Being promising candidates for anodes in lithium-ion batteries (LIBs), transition metal oxide anodes utilizing the so-called conversion mechanism principle typically suffer from the severe capacity fading during the 1st cycle of lithiation-delithiation. Also we report on the atomistic insights of the GN energy storage as revealed by in situ TEM (Fig. 1d). The lithiation process on edges and basal planes is directly visualized, the pyrrolic N "hole" defect and the perturbed solid-electrolyte-interface (SEI) configurations are observed, and charge transfer states for three N-existing forms are also investigated. In situ HRTEM experiments together with theoretical calculations provide a solid evidence that enlarged edge {0001} spacings and surface "hole" defects result in improved surface capacitive effects and thus high rate capability and the high capacity is owing to short-distance orderings at the edges during discharging and numerous surface defects; the phenomena could not be understood previously by standard electron or X-ray diffraction analyses.

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International Center for Materials Nanoarchitectonics (MANA)
National Institute for Materials Science (NIMS)

1-1 Namiki, Tsukuba, Ibaraki 305-0047, JAPAN
Phone: +81-29-860-4709, Fax +81-29-860-4706
E-mail: mana@nims.go.jp
URL: http://www.nims.go.jp/mana/

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