# MANA Progress Report Research Digest 2014



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

National Institute for Materials Science (NIMS)

## Preface

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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 Initiative (WPI Program) of Japan's Ministry of Education, Culture, Sports, Science and Technology (MEXT). Our vision is to "create a better future for humanity by supporting the development of new materials through opening up a new paradigm of nanotechnology." We believe that conceptual innovation must be brought into the nanotechnology developed to date. We express the concept of this innovated nanotechnology by the term nanoarchitectonics.

MANA achieved remarkable research results in the past 7 years. MANA's excellence is apparent from several indicators. For example, A) the number of papers in the world's top 1% by the number of citations has reached 80, B) MANA has achieved a very high field-weighted citation impact (FWCI) — a new indicator devised by Elsevier to fairly compare the quality of papers published by interdisciplinary research institutions — of 2.5 (both statistics are based on papers published between 2008 and 2013), and C) the average impact factor (IF) of journals in which MANA researchers have published papers is very high 5.24 (based on papers published in 2012). These figures far exceed those of many other world-class research institutes.

The MANA Progress Report consists of two booklets named "Research Digest 2014" and "Facts and Achievements 2014". This booklet "Research Digest 2014" presents MANA research activities and the other booklet "Facts and Achievements 2014" serves as a summary to highlight the progress of the MANA project.



# **MANA Research Digest 2014**

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

## **Nano-Materials Field**

Fakayoshi SASAKI (Field Coordinator, PI)	·····7
Inorganic Nanosheets	
Katsuhiko ARIGA (PI)	····· 8
Supramolecular Materials	
Yoshio BANDO (MANA Chief Operating Officer, PI)	9
Inorganic Nanostructured Materials	
Foyohiro CHIKYOW (PI)	- 10
Nano Electrics and Related Materials	
Omitri GOLBERG (PI)	11
Pioneering Opto-Mechano-Electrical Nano-Tests in TEM	
Lhong Lin WANG (Satellite PI)	12
Nanogenerators as a New Energy Technology	
Minoru OSADA (API)	13
Nanosheet Electronics	

## Nano-System Field

Iasakazu AONO (MANA Director-General, Field Coordinator, PI)	
Nano-System Architectonics	
ames K. GIMZEWSKI (Satellite PI)	
MANA Brain: Neuromorphic Atomic Switch Networks	
suyoshi HASEGAWA (PI)	
Atomic Electronics for Future Computing	
Xiao HU (PI)	
Superconductivity as a Platform for Novel Functionality	
Christian JOACHIM (Satellite PI)	
Surface Atomic Scale Logic Gate	
omonobu NAKAYAMA (PI)	
Integration of Nano Functionality for Novel Nanosystems	

Hideaki TAKAYANAGI (Satellite PI)	····· 20
Mesoscopic Superconductivity and Quantum Information Physics	
Kazuhito TSUKAGOSHI (PI)	······ 21
Electrostatically Reversible Polarity Switching in Ambipolar α-MoTe <sub>2</sub> Transistors	

## Nano-Power Field

Jinhua YE (Field Coordinator, PI)   22
Nanoarchitectonics of Hybrid Artificial Photosynthetic System
Kazunori TAKADA (PI)23
Solid-State Batteries
Kohei UOSAKI (PI)24
Construction of Interphases with Atomic/Molecular Order for Efficient
Conversion of Energy and Materials
Omar M. YAGHI (PI)25
Reticular Materials
David BOWLER (Satellite API)   26
Dye-Sensitized Solar Cells and Core-Shell Nanowires

## Nano-Life Field

Takao AOYAGI (Field Coordinator, PI)	
Smart Nano-Biomaterials	
Guoping CHEN (PI)	
Creation of Nanostructured Scaffolds Using Single-Walled Carbon Nanotubes and	
Their Cellular Effects	
Yukio NAGASAKI (Satellite PI)	
Nanotherapeutics Based on Redox Polymer Nanoarchitectonics	
Françoise M. WINNIK (Satellite PI)	
Nanoarchitectonics-Driven Interfaces and Nanoparticles for Therapeutic Applications	

## **Group Leaders (11)**

Naoki FUKATA (Nano-Materials Field)	
Next-Generation Semiconductor Nanodevices	
Nobutaka HANAGATA (Nano-Life Field)	
Development of Nanomedicines	
Masanori KIKUCHI (Nano-Life Field)	
Bioactive Ceramics Materials	
Hisatoshi KOBAYASHI (Nano-Life Field)	
Materials for Functional Nanomedicine	
Takao MORI (Nano-Materials Field)	
Functionalization of Atomic Network Materials	
Tadaaki NAGAO (Nano-System Field)	
Control of the Infrared Light in Nanospace	
Takashi SEKIGUCHI (Nano-Materials Field)	
Characterization and Control of Defects in Semiconductors	
Akiyoshi TANIGUCHI (Nano-Life Field)	
Development of Sensor Cells for Nanomaterials Safety Evaluation	
Yoshitaka TATEYAMA (Nano-Power Field)	
Nano-System Computational Science	
Kazuya TERABE (Nano-System Field)	······ 40
In-Situ Bandgap Tuning of Graphene Oxide Achieved by Electrochemical Bias	
Akiko YAMAMOTO (Nano-Life Field)	41
Effect of Living Cells on the Biodegradation of Mg Alloys	

## **MANA Independent Scientists (14)**

Ryuichi ARAFUNE	
Laser-Based Inelastic Photoemission Spectroscopy	
Alexei A. BELIK	43
Search for New Ferroelectric, Magnetic, and Multiferroic Materials Using	
High-Pressure Technique	
Ryoma HAYAKAWA	
Interface Engineering for Improving Optical Switching in a Diarylethene-Channel Transisto	or
Joel HENZIE	
Non-Precious Metal Bi-Functional Colloidal Catalysts for Oxygen Evolution and	
Reduction Reactions	
Takeo MINARI	46
All-Solution-Processed Fabrication of High Performance Thin-Film Electronic Devices	
Satoshi MORIYAMA	······ 47
Quantum Devices in Nanomaterials	
Jun NAKANISHI	48
Development of Photoresponsive Biointerfaces	
Takashi NAKANISHI	
Development of Optically and Optoelectronically Active Molecular Liquid Materials	
Liwen SANG	
Novel Solar Cell Concept with a Super-wide Response Spectrum Based on III-V	
Nitride Semiconductors	
Naoto SHIRAHATA	51
Green Nanochemistry: Bandgap Engineering for Group IV Nanostructures	
Satoshi TOMINAKA	52
Toward the Development of Future Materials for Fuel Cells	
Katsunori WAKABAYASHI	53
Theoretical Research on Electronic Properties of Nano-Carbon Systems and	
Atomically Thin Materials	
Thin MaterialsYusuke YAMAUCHI	54
Tailored Synthesis of Nanoporous Carbons with Various Architectures	
Genki YOSHIKAWA	55
Development of MSS-Type Nanomechanical Sensors for Real-Time Gas Identification	
on Mobile Platforms	

## **ICYS-MANA Researchers (9)**

Sudipta DUTTA	
Tuning Electronic Properties of Atomically Thin Nanomaterials: Theoretical Perspective	
Hicham HAMOUDI	57
Self-Assembled Monolayers Toward New Dynamic and Magnetoresistive RAM	
Yohei KOTSUCHIBASHI	58
Polymeric Nanomaterials for Biomedical Application	
Huynh Thien NGO	
Functionality Driven Application of Porphyrinoid Conjugates and Nanowires	
Kota SHIBA	
Development of Optimized Receptor Layers on Gas Sensing Devices for	
Non-Invasive Breath Diagnostics	
Dai-Ming TANG	61
Nanomechanical Cleavage of Molybdenum Disulphide Atomic Layers	
Xi WANG	
N-doped Graphene-Based Electrodes for the Energy Application and their Storage	
Mechanisms at Atomic Scale	
Xue-Bin WANG	
Nanosheets of Boron-Carbon-Nitrogen System for Energy and Composite Applications	
Hamish Hei-Man YEUNG	
Towards Metal-Organic Framework Nanoarchitectonics: Fundamentals of Synthesis and	
Design	

## Inorganic Nanosheets

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#### 1. Outline of Research

Graduate Student

We aim at synthesizing 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 the exotic 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 species (organic modules, metal complexes, clusters...). Particularly we attempt to realize new or sophisticated functions by cooperative interaction between nanosheets themselves or between nanosheets and other functional modules.



Fig. 1. Conceptual explanation of the research plan.

#### 2. Research Activities

(1) Electrochemical supercapacitors using redoxable nanosheets and graphene.<sup>1)</sup>

We have fabricated for the first time a genuine superlattice nanocomposite through molecular-scale heteroassembly of cationic transition metal (Co-Al, Co-Ni, etc.) hydroxide nanosheets and anionic graphene. The combination of redoxable nanosheets directly adjacent with conductive graphene can greatly improve the charge transfer efficiency. The resultant hybrid supercapacitors based on the nanocomposites show both high capacity (~650 F/g) and high power rate (Fig. 2). An almost ideal capacitive behavior up to ~100 Hz, comparable to that of graphene electrodes, has been achieved. Such a superfast charging and discharging ability validates a potential huge energy output within a very short time scale, i.e., sub-second.



Fig. 2. A schematic model of the charge transfer from redoxable hydroxide nanosheets to conductive graphene in the superlattice composite (left) and typical galvanic chargedischarge curves (right).

#### (2) All-Nanosheet-Nanocapacitors.<sup>2)</sup>

We have fabricated a metal-insulator-metal nano- structure by assembling layer-by-layer conducting and dielectric nanosheets of  $Ru_{0.95}O_2^{0.2-}$  and  $Ca_2Nb_3O_{10}^{-}$ , respectively, through electrostatic self-assembly and Langmuir Blodgett processes. All the characterization data including cross-sectional TEM support the successful construction of the sandwich nanostructure with a thickness of ~28 nm (Fig. 3). The MIM device thus fabricated worked as a nanocapacitor, showing dielectric/insulating performance that are far superior to currently available devices.



Fig. 3. A cross-sectional TEM image of the MIM nanostructure of Ru<sub>0.95</sub>O<sub>2</sub>/Ca<sub>2</sub>Nb<sub>3</sub>O<sub>10</sub>/Ru<sub>0.95</sub>O<sub>2</sub> (left) and its dielectric performance (right).

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## Supramolecular Materials

MANA Principal Investigator MANA Scientist

MANA Research Associate

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#### 1. Outline of Research

Functional materials have been wisely constructed via bottom-up approaches as seen in preparation of molecular and nano patterns, complexes, and nanomaterials organized nano- and microstructures, and function materials. We are working in exploratory research for innovative materials and sensing systems based on supramolecular concept.

#### 2. Research Activities

#### (1) Novel Sensing System.

We reported chiral guest binding as a probe of prototropic tautomerism and macrocyclic inversion in a highly conjugated tetrapyrrole studied using <sup>1</sup>H NMR spectroscopy in conjunction with mandelic acid as the chiral guest.<sup>1)</sup> Both tautomerism and macrocycle inversion can be influenced in a non-trivial way depending on temperature and the respective concentrations of tetrapyrrole host, chiral guest or water. Chirality of the interacting guest is the key feature since it permits separation and detailed observation of macrocyclic inversion and tautomerism. Based on this, a methodology was developed to identify and characterize the dynamic processes. Our observations suggest that yields of products (e.g., of asymmetric reactions) can be affected by reactivity of functional groups (in molecules undergoing tautomerism or inversion) by varying solution properties including reagent concentrations and impurities such as water. This work establishes a connection between the important chemical concepts of chirality, tautomerism, and macrocyclic dynamics.

NAD(P)H is a critical component of cellular energy metabolism operating as an electron carrier. We have developed a novel fluorescent ubiquinone-rhodol derivative (UQ-Rh) as a probe for NAD(P)H.<sup>2)</sup> Using the artificial promoter  $[(\eta^{5}-C_{5}Me_{5})Ir(phen)(H_{2}O)]^{2+}$ , intracellular activation and imaging of NAD(P)H were successfully demonstrated.

The accident at the Fukushima Daiichi nuclear power plant, which was one of the most serious adverse effects of the Great East Japan Earthquake, was accompanied by the



Fig. 1. Fluorescent imaging of distribution of cesium within plant cells.

release of a large quantity of radioactive materials including <sup>137</sup>Cs to the environment. In a previous report, we developed and proposed a cesium (Cs) fluorescent probe, "Cesium Green," that enables the detection of cesium carbonate particles by spraying an alcoholic solution of the Cesium Green probe. In this paper, the sensing activity of this probe was investigated for its selectivity (by using an optode method) and for its application to detect micrometer-sizes Cs particles. Cesium Green was also assessed for its use in plant cellular imaging of Cs localization in Arabidopsis.<sup>3)</sup> Cesium Green enabled high-resolution Cs imaging of Cs-containing particles and of Cs contained in plants (Fig. 1).

(2) Nobel Supramolecular Materials.

Linear  $\pi$ -gelators spontaneously self-assemble into entangled network fibers in which the molecules are arranged perpendicular to the fiber long axis. However, manipulating orientation of the same gelator molecules in a direction parallel to the long axes of the one-dimensional (1D) structures remain challenging. We demonstrated that at the air-water interface, an oligo(*p*-phenylene vinylene) (OPV) derived  $\pi$ -gelator forms aligned nanorods of 340  $\pm$ 120 nm length and  $34 \pm 5$  nm width in which the gelator molecules are reoriented parallel to the long axis of the rods.<sup>4)</sup> The orientation change of the molecules results in distinct excited state properties upon local photoexcitation as evidenced by near-field scanning optical microscopy (NSOM). A detailed understanding of the mechanism by which excitation energy migrates through these 1D supramolecular molecular assemblies might help in the design of supramolecular structures with improved charge transport properties.

We demonstrated the thermal conversion of onedimensional (1D) fullerene (C<sub>60</sub>) single crystal nanorods and nanotubes into nanoporous carbons with retention of the starting 1D morphologies.<sup>5)</sup> 1D C<sub>60</sub> crystals are heated directly at very high temperature (up to 2000 °C) in vacuum, yielding a new family of nanoporous carbons having  $\pi$ -electron conjugation within the sp<sup>2</sup>-carbon robust frameworks. These new nanoporous carbons show excellent electrochemical capacitance and superior sensing properties for aromatic compounds compared to commercial activated carbons.

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## **Inorganic** Nanostructured Materials

MANA Principal Investigator (MANA Chief Operating Officer) MANA Scientist MANA Research Associate

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## 1. Outline of Research

Graduate Student

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. To fulfill our goal, a full set of instruments for synthesis and characterizations of nanomaterials are set up, such as induction furnace, transmission electron microscope *etc.* These enable the effective control of the nanomaterials fabrication, and the further investigation of their energy storage capability and optoelectronics properties for applications in hydrogen storage, field emission display and UV light detection.

#### 2. Research Activities

# (1) Large-Scale Synthesis of Porous Boron Nitride and Its Application in Hydrogen Storage.<sup>1,2)</sup>

We successfully develop a brand new solid reaction (Fig. 1a) to directly fabricate highly water-soluble and porous boron nitrides via thermal substitution of C atoms with boric acid substructures in graphitic carbon nitrides. The fabricated materials can form stable and highly transparent water solutions with high concentration.

In addition, highly porous, sponge-like boron nitride (BNMSs) with ultrahigh surface areas up to 1900 m<sup>2</sup>g<sup>-1</sup>, are achieved by a facile, one-step, template-free reaction of boric acid and dicyanamide (Fig. 1b). It is demonstrated that these microporous materials (with pore widths of 1.0 nm) display comparatively high and reversible H<sub>2</sub> sorption capacities from 1.65 to 2.57 wt % at 1 MPa and –196 °C on a material basis.



Fig. 1. (a) Thermal substitution reaction between g-C<sub>3</sub>N<sub>4</sub> and boric acid for growing hydroxylated BN structure. (b) HRTEM images of BN microsponges and their hydrogen adsorptiondesorption isotherms.

(2) Boron Nanowire Patterns for Field Emission Display.<sup>39</sup>

Large-scale patterned boron nanowire (BNW) arrays have been successfully prepared on a  $2 \text{ cm} \times 1.5 \text{ cm}$  substrate utilizing the sole base-up growth mode (Fig. 2). These

BNWs have a mean length of 6  $\mu$ m and an average diameter of 35 nm. Field emission measurements on patterned BNWs show that they not only have a low turn-on (4.3 V/ $\mu$ m) and threshold field (10.4 V/ $\mu$ m) but also possess very high emission site distribution uniformity (81.8%) and brightness distribution uniformity (88.9%).



Fig. 2. (a) SEM images of large area BNW patterns. (b) The field emission performance of the BNW patterns.

#### (3) Flexible Ultraviolet Photodetectors Based on Branched ZnS-ZnO Heterostructure Nanofilms.<sup>4)</sup>

We successfully synthesized a branched architecture composed of ZnS backbones and ZnO branches by combining a thermal evaporation growth and a hydrothermal process (Fig. 3). The application of nanofilm networks made of as-fabricated ZnS-ZnO nanostructures as a flexible UV photodetector was demonstrated. The devices exhibited excellent characteristics: tunable spectral selectivity, widerange photo response, fast response speed, and excellent environmental stability. In addition, the devices are able to decently bear external mechanical forces, suggesting their great potential applications.



Fig. 3. (a) Optical image and micrograph of the devices on PET. (b) SEM image of branched ZnS-ZnO heterostructures. (c) Timedependent response of the device to 320 nm light.

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## Nano Electrics and Related Materials

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



#### 1. Outline of Research

The wide-bandgap semiconductor zinc oxide has attracted interest recently as an alternative to III-nitrides for the development of optoelectronic devices operating in blue and UV regions owing to the large exciton binding energy of 60 meV and direct bandgap of 3.37 eV.<sup>1,2)</sup> Many of the physical properties of ZnO are similar to those of GaN. ZnO offers some unique characteristics such as simple processing because of the amenability to chemical wet etching and relatively low raw material cost. Most importantly, non polar epitaxial growth of ZnO and GaN thin films can contribute to suppress the "Stark Effect" which reduce the light emission efficiency by internal electric field in compound semiconductor. In this report, a nonpolar n-ZnO/ i-ZnO/p-GaN heterostructure LEDs were fabricated using AlN and MnS as buffer layers to demonstrate UV LED by ZnO/GaN heterojunction.

#### 2. Research Activities

#### (1) AlN/MnS/Si(100) template substrate for non polar ZnO/ GaN LED.

MnS and AlN buffer layers along were grown on Si(100) substrates by PLD using a KrF excimer laser (Coherent LPX200; 248 nm). A 50-nm-thick MnS layer was first deposited on the Si substrate at a substrate temperature of 600°C. The MnS film was then post-annealed for 30 min at 600 °C. After annealing, 20 nm of AlN was deposited directly on top of the MnS layer at 600°C and, followed by post-annealing for 5 min. XRD showed an epitaxial growth of AlN (11-20) on Si(100) with MnS(100) buffer layer.<sup>3,4)</sup>

# (2) Non polar ZnO/GaN heterojunction LED on Si with GaN/MnS buffer.

A 1.0  $\mu$ m thick GaN buffer layer was grown on the AlN/ MnS-buffered Si(001) to reduce the defect density. Subsequently another 1.0  $\mu$ m thick GaN layer doped with Mg was grown on the GaN buffer layer to make p-type GaN layer. Both the GaN and Mg doped GaN layers were grown by MOCVD at 1000°C. After the growth, the sample was loaded into another PLD chamber for the growth of n-ZnO



Fig. 1. Nonpolar n-ZnO/i-ZnO/p-GaN heterostructure LEDs fabricated using AlN and MnS as buffer layers.

and i-ZnO layers. The thicknesses of the films were 0.3 and 0.6µm. A schematic illustration of the fabricated nonpolar n-ZnO/i-ZnO/p-GaN heterostructure LEDs is shown in Fig. 1. The n-ZnO/i-ZnO/p-GaN heterostructure LEDs were fabricated by initially making an ohmic contact on the n-ZnO layer by simply depositing 200-µm-diameter Ti and Au bilayer electrodes using a shadow mask and electron beam deposition (EBD). The typical thicknesses of the Ti and Au were 10 and 100 nm, respectively. The n- and i-ZnO layers were chemically etched to expose the p-GaN layer using 10% HCl aqueous solution. This technique allows the ZnO to be etched rapidly, while the GaN is resistive to the acidic environment. Another ohmic contact was made on the p-GaN by depositing Ni and Au bilayers with thicknesses of 10 and 100 nm, respectively. Strong and sharp UVemission centered at 390 nm was observed when the nonpolar n-ZnO/ i-ZnO/p-GaN hetero structure LEDs were operated under reverse bias at 50V and 10 mA, as shown in Fig. 2.



Fig. 2. Strong and sharp UV emission centered at 390 nm was observed from the nonpolar n-ZnO/i-ZnO/p-GaN hetero structure LED.

In summary, nonpolar a-plane ZnO films have been successful grown on AlN/MnS-buffered Si(001) by PLD. The epitaxial relationship between the ZnO film and AlN/MnS-buffered Si substrate was found to be ZnO(11-20)/AlN(11-20)/MnS(001)/Si(001). The nonpolar n-ZnO/i-ZnO/p-GaN hetero structure fabricated on the AlN/MnS-buffered Si(001) by employing PLD for the ZnO and MOCVD for the p-GaN showed strong UVemission at 390 nm under forward and reverse bias. The present work will be helpful for designing UV–blue LEDs with nonpolar ZnO/GaN hetero epitaxial films on Si substrates.

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## Pioneering Opto-Mechano-Electrical Nano-Tests in TEM

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#### 1. Outline of Research

We developed a principally new set of experiments inside a high-resolution transmission electron microscope (HRTEM), Fig. 1, aimed at the analysis of intriguing optomechano-electrical tripling phenomena within diverse individual zero-, one- and two-dimensional nanomaterials, e.g. nanoparticles, nanotubes, nanowires, nanobelts, nanoscale hybrids and graphene-like nanosheets, nanostructures. The light of any pre-selected wavelength and/or frequency is coming inside the TEM column through a threaded optical fiber (inside the side entry holder). This new technique allows us to analyze the combined effects of lightening and mechanical deformation (e.g. bending, compression, tension) on photocurrents generated inside a bunch of advanced nanomaterials, like Si (Fig. 2), CdS, ZnS and ZnO nanowires, heterojunctions between them, TiO<sub>2</sub> nanoparticles, BN nanotubes, B-C-N nanosheets, MoS<sub>2</sub> graphene-like nanostructures and many others, under the highest spatial (0.17 nm) and temporal resolutions which are particularly achieved with HRTEM.



Fig. 1. (a) Designed experimental setup inside a high-resolution TEM for the first opto-mechano-electrical tests on nanomaterials; and (b) A photo of a TEM side-entry holder tip frame with a laser light of pre-determined wavelength and frequency shining on a nanostructured sample.

#### 2. Research Activities

#### (1) CdS-ZnO hybrids for optoelectronics studied in TEM.

Design and rational synthesis of semiconducting nanowire building blocks with well-defined structures and compositions are the central tasks for the fabrication of nanoelectronic and optoelectronic devices with unique properties. We have successfully synthesized CdS/ZnO branched heterostructures by combining thermal vapor deposition and hydrothermal method. Drastic optoelectronic performance enhancement of such heterostructures was revealed, compared to plain CdS nanobelts, as documented by *in-situ* optoelectronic studies.<sup>1)</sup> Furthermore, flexible thin-film based photodetectors based on standard CdS nanobelts and newly prepared CdS/ZnO heterostructures were fabricated on flexible PET substrates, and comparative photocurrent and photo-responsivity measurements thoroughly verified the *in-situ* TEM results. The CdS/ZnO branched heterostructures were found to have three main advantages over standard CdS nanobelts for optoelectronic applications. These namely are: (i) enhanced photocurrent to dark current ratio, (ii) improved responsivity, and (iii) shorten response time.

#### (2) CdS-Si p-n junctions created and analyzed in HRTEM.

In recent years, many nanowire-based devices, e.g. transistors, photodetectors, and logic circuits have successfully been fabricated on substrates using various lithography techniques. In contrast, on-demand flexible manipulation with two or more individual nanowires with a nanoscale precision and immediate creation of axial heteroarchitectures made of them (for the straightforward optoelectronic tests) have never been attempted. Herein we developed a direct in situ TEM approach toward fabrication of individual axial nanowire junctions (perfectly highlighting the real nanoarchitectonics concept which is in the center of MANA). For the first time, in situ and in-tandem highresolution structural characterizations, and optoelectronic measurements reveal the peculiar photosensing properties of the single-crystalline axial CdS/p-Si nanowire junctions.<sup>2)</sup> The junctions possess good selectivity toward the light frequencies higher than those of the yellow range. In addition, the junctions exhibit photocurrent saturation effect; this could be utilized in low consumption light intensity sensing applications due to corresponding current limitations and high stability to possibly unreliable bias.



Fig. 2. (a) TEM image depicting an individual Si nanowire of 46 nm width and 213 nm length placed between gold and tungsten probes inside HRTEM and illuminated with a laser light; and (b) the corresponding I-V curves demonstrating a clear photoresponse of the wire.

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## Nanogenerators as a New Energy Technology

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Guang Zhu Sihong Wang



#### 1. Outline of Research

Harvesting mechanical energy from ambient environment and human body has attracted increasing interest for nano-scale self-powered electronic devices and large-scale energy needs. The various physical mechanisms, such as electromagnetic, electrostatic, and piezoelectric effects, have been utilized to harvest mechanical energy. Recently, triboelectric nanogenerator (TENG) has been invented as a new technology to harvest mechanical energy, which is based on contact electrification effect and electrostatic induction. Various applications of TENG have been demonstrated, such as self-powered chemical sensor, electrodegradation, and powering commercial LEDs.

Triboelectric nanogenerators are based on the coupling of two effects: contact electrification and the electrostatic induction. The contact electrification is a universally-existing phenomenon in the nature and people's living life, and has been known for thousands of years. It describes a phenomenon that a material/surface becomes electrically charged after it gets into contact with a different material/surface. The generated triboelectric charges on a dielectric surface can be preserved for a long time, which thus serve as the induction source for the electricity generation process in TENGs. Under the driving of external mechanical motions, the relative position of the Triboelectrically charged surface will change periodically in a TENG device, which will lead to the periodic variation of the induced potential difference between the two electrodes. In order to keep the electrostatic equilibrium between the two electrodes, the free electrons in the electrodes will be driven to flow back and forth to screen



Fig. 1. The four fundamental modes of triboelectric nanogenerators: (a) vertical contactseparation mode; (b) in-plane contactsliding mode; (c) single-electrode mode; and (d) freestanding triboelectric-layer mode.

the induced potential difference. In this way, the applied mechanical energy is converted into electricity. With different configurations of the electrodes and/or different moving manners of the triboelectric layers to realize the electrostatic induction process, four fundamental modes of TENGs have been established (Fig. 1). They are, respectively, vertical contact-separation mode, lateral sliding mode, single-electrode mode and freestanding triboelectric-layer mode

#### 2. Research Activities

We have increased the output energy and operation frequency of a triboelectric nanogenerator by using a twogrounded-electrodes approach. For such two-channel TENG, the two electrodes are simultaneously grounded to form two electrical channels with the ground, which can collect double charges, and provides double output energy at a load lower than 1 M $\Omega$ . For single-channel TENG, the two electrodes are alternately grounded through a selftriggered vibrating switch. About 30 current peaks with an output frequency of 50 Hz appear in a single cycle as the motion triggering frequency being 2 Hz, and the output frequency can be modulated from 25 to 50 Hz by adjusting the length of the vibrating switch. The output energy of the single-channel TENG is remarkably enhanced at a load lower than 10 M $\Omega$  compared to the ungrounded TENG, and the enhancing ratio is more than 100 at a load of 100 k $\Omega$ . As the LEDs are driven by the single-channel TEG-TENG, the lighted duration time is enhanced for about 3 times. The results indicate that the TENG is a new strategy for effective use of the energy harvested from our living environment.<sup>1-5</sup>

Further, we developed a new theoretical simulation method for integrated TENG systems through integrating the equivalent circuit model of TENG into SPICE software. This new simulation method was validated by comparing its results with analytical solutions in some specific TENG systems. Finally, we employed this new simulator to analyze the performance of an integrated TENG system with a power management circuit. From the study of the influence of different circuit parameters, we outline the design strategy for such kind of TENG systems.

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## Nanosheet Electronics

#### Associate Principal Investigator Minoru OSADA

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#### 1. Outline of Research

Two-dimensional (2D) materials with atomic scale thickness are emerging as a new frontier of materials science. The discovery of graphene can be considered as a defining point in the research and development of truly 2D material systems. This breakthrough has opened up the possibility of exploring the fascinating properties of non-graphene 2D nanosheets. In particular, 2D inorganic nanosheets will offer new properties and novel applications beyond graphene. We are working on the creation of 2D oxide nanosheets and the exploration of their novel functionalities in electronic applications.

#### 2. Research Activities

#### (1) Controlled Doping of Oxide Nanosheets.<sup>1)</sup>

To date, 2D oxide nanosheets have mainly been produced through an exfoliation process based on the intrinsic layered structure characteristic of their bulk counterparts, which definitely hinders the further study of oxide nanosheets. To expand the utility of 2D oxide nanosheets, the electronic properties must be tailored through lattice engineering and/ or doping process. For tailoring spinelectronic materials, we developed new technique for controlled magnetic doping of semiconductor  $Ti_{1-\delta}O_2$  nanosheets. A key feature of this new preparation is the use of designed layered titanates as starting materials (Fig. 1). The composition of the host layers is maintained in the subsequent exfoliation process, which is very helpful in the rational design of nanosheets.



Fig. 1. Controlled doping in magnetic nanosheets (Ti<sub>1-xy</sub>Fe<sub>x</sub>Co<sub>y</sub>O<sub>2</sub>).

Through this controlled doping, we achieved exquisite control of electronic and ferromagnetic properties in  $Ti_{1-6}O_2$  nanosheets and successfully developed half-metallic ferromagnets based on  $Ti_{1-x}Fe_xCo_yO_2$  nanosheets.

#### (2) High-k Oxide Nanosheets and Their Applications.<sup>2-5)</sup>

Despite significant advances in graphene-like 2D nanosheets, it remains a challenge to explore high-k dielectric counterparts, which have great potential in new 2D electronics. Oxide nanosheets may be the perfect solution as 2D dielectrics. Titania- or perovskite-based nanosheets (Ti<sub>2</sub>NbO<sub>7</sub>, (Ca,Sr)<sub>2</sub>Nb<sub>3</sub>O<sub>10</sub>) realized the highest permittivity  $(\varepsilon_r > 200)$  of all known dielectrics in the ultrathin region (< 10 nm).<sup>2)</sup> We also found that these nanosheets retain both size-free high- $\varepsilon_r$  characteristic and high insulation resistance at high temperatures up to 250 °C (Fig. 2).34 Notably, nanosheet-based capacitors exhibited an unprecedented capacitance density (~100  $\mu$ F/cm<sup>2</sup>), which was 1000 times higher than that of state-of-the art ceramic condensers.<sup>5)</sup> The simultaneous improvement of  $\varepsilon_r$  and thermal stability in high-k nanodielectrics is of technological importance, and oxide nanosheets have great potential for a rational design of future capacitors and energy storage devices.



Fig. 2. Dielectric response of nanosheet-based capacitor.

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## Nano-System Architectonics

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#### 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:

- Novel nanochemical control: 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.
- New functionality by organic integration and mutual linkage of individual nanostructures under external stimulus, 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 systems: For example, elucidation of the difference in electronic states between electron-doped and hole-doped high-temperature superconductors.

In the following, subjects 1) and 2) will be discussed in more detail.

Aiming at the realization of single-molecule electronics, we developed a novel method for connecting single



Gold electrodes Diacetylene layer on h-BN

Fig. 1. (a) Optical microscope image of electrodes fabricated on a hexagonal boron nitride (h-BN) surface. (b) Atomic force microscopy (AFM) image of it. Single polydiacetylene chains have been fabricated between the electrodes. conductive polydiacetylene chains to single organic molecules, which we named "chemical soldering". 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 fabricated gold electrodes on an insulating hexagonal boron nitride (h-BN) substrate by electron beam lithography, and form a self-assembled layer of diacetylene molecules between the electrodes. Then, as shown in Fig. 1, we succeeded in fabricating single polydiacetylene chains between the electrodes, by thermal polymerization of the diacetylene molecules.



Fig. 2. (a) Reversible semiconductor-insulator transition caused by creation and healing of lattice defects in SnO<sub>2</sub> microrod by stress and voltage. (b) Novel UV photo-sensitivity of SnO<sub>2</sub> microrod device by the reset process (bending, straitening, applying voltage).

In subject 2), new functionality was achieved by creation and healing of lattice defects in a single-crystal SnO<sub>2</sub> microrod. The microrod exhibited reversible and nonvolatile semiconductor-insulator transition under the application of mechanical strain and voltage (Fig. 2a). To understand the origin of this transition, we studied lattice defects of a SnO<sub>2</sub> wire under mechanical strain, using transmission electron microscope (TEM) and photoluminescence (PL) spectroscopy.<sup>2)</sup> TEM studies indicated slip planes in mechanically bent SnO<sub>2</sub> nanowires. The PL spectra of the bent SnO<sub>2</sub> microrods showed strong visible emission, caused by mechanical stress-induced defects in the band gap. The SnO<sub>2</sub> microrod device also showed potentials as a UV photoconductor with high gain ( $\sim 1.5 \times 10^{9}$ ) and quick recovery speed (Fig. 2b). The recovery speed was induced by a novel "reset" process: bending and straightening the microrod and subsequently applying a voltage pulse. The results demonstrate a solution to the persistent photoconductivity (PPC) problem, which has been known in wide-band-gap semiconductors.

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## MANA Brain: Neuromorphic Atomic Switch Networks

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James K. GIMZEWSKI



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#### 1. Outline of Research

Self-organized complex systems are ubiquitous in nature, and the structural complexity of these natural systems can be used as a model to design new classes of functional nanosystems based on interconnected networks of interacting units. Nanoarchitectonics has been applied to the production of a self-organized, complex device known as an Atomic Switch Network (ASN). Fabricated through a merger of top-down and bottom-up methods, ASN devices comprising nanoscale elements represent a unique approach to the fields of natural and cognitive computing, methods which rely on non-algorithmic learning to address problems in which complex datasets are constantly changing, incomplete, or subject to errors.

#### 2. Research Activities

The ASN device architecture, comprising interacting nonlinear elements seeks to (1) explore scaling in selforganized systems (2) study complex, emergent behaviors and (3) harness operational dynamics toward implementation of reservoir computing - a universal computational paradigm mimicking biological neural networks in artificial computing environments.

#### (1) Next-generation devices.

As in natural systems, structural complexity of the ASN plays a role in its functionality. Devices have been fabricated in order to maximize connectivity and functional diversity while retaining control over topology and operational reproducibility. Integration with a purpose-built multielectrode array, shown in Fig. 1, has provided a means to stimulate and monitor the network response with high spatial and temporal precision.



Fig. 1. A 16 channel multi-electrode array (left) on a silicon substrate enables electrical characterization of the ASN (right).

#### (2) Nonlinear spatiotemporal dynamics.

The unique behaviors observed in the ASN device arise from the recurrent connectivity amongst atomic switches within the network whose operational properties provide a basis for the memorization and transformation of information. In addition, their inherent volatility enables a continuous energetic redistribution due to the dynamics of filament formation and dissolution resulting in patterns of robust electrical activity that are distributed throughout the network in space and time as seen in Fig. 2.

Interactions between elements within the ASN produce extensive fluctuations and nonlinear transformations not present in single switches including: 1/f noise, temporal metastability, and distributed voltage fluctuations across all spatiotemporal scales; properties indicative of a critical state where correlations and mutual information are maximized amongst all elements in the network.



Fig. 2. Spatial mapping of local and distributed activity in the ASN is highlighted by real-time multichannel maps of local electrical potential where each row (a-c) represents activity of the network for 3 ms under an applied DC bias.

#### (3) Natural computing.

As computational tasks become increasingly difficult, the ability to solve complex systems is necessary. The capacity for non-linear transformation of information serves to increase the dimensionality of the network response; thereby increasing output separability and the computational capacity. Building on prior efforts to perform reservoir computation, various benchmark logic operations have been successfully implemented using ASN devices including AND, NOR, NAND XOR without algorithmic preprogramming as seen in Fig. 3.



Fig. 3. Performance of the XOR, a non-linearly separable task using ASN devices in the reservoir computing paradigm.

These results further indicate that ASN devices provide the balance of intrinsic memory capacity and non-linear operations required for advanced computing applications and offer the possibility of creating task-specific devices for natural computing.

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## Atomic Electronics for Future Computing

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#### 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 are using atomic switches, developed by ourselves, in which diffusion of metal cations/atoms and their reduction/oxidation processes are controlled for turning on/off operations. In order to accomplish the purpose, we will conduct 1) basic research on nanoionic phenomena, 2) developing new atomic switches showing the novel functions based on the basic research, 3) developing nanofabrication technique for making the atomic switches, 4) demonstration of novel operation of the atomic switches and basic circuits/systems using them.

#### 2. Research Activities

#### (1) Basic Researches on Nanoionic Phenomena.

Atomic switches show volatile and nonvolatile selective switching both in two-terminal<sup>1)</sup> and three-terminal<sup>2)</sup> structures. This is in contrast to that the conventional devices show only one of the two switching modes. In order to reveal the mechanism, we investigated nanoionic phenomena, such as dissolution of metal cations into an ionic transfer material and their diffusion in the material.<sup>3)</sup> We also developed a new method for finding the position of conductive filaments hidden under top electrodes, enabling the cross-sectional TEM observation of a conductive filament formed in an actual device operation.<sup>4)</sup> The observation confirmed that nucleation



Fig. 1. (a) TEM image of a conducting point showing a dome-shaped structure. (b) EDX map of Cu. (c) Model of the filament formation.

of a metal cluster followed by spontaneous filament formation occurs in the switching-on process. Cross-sectional TEM images and the model we proposed<sup>5)</sup> are shown in Fig. 1.

#### (2) Pattern Recognition using Atomic Switches.<sup>6)</sup>

We proposed new pattern recognition model using the Hopfield-type of neural network whose connection matrix is represented by each height of Ag protrusions of multi-step atomic switches. In a normal pattern recognition model, the most similar pattern to input pattern is retrieved by the neural network among patterns stored in a learning stage.

Fig. 2 shows that in our model the original (noiseless) pattern can be retrieve even though we displayed only the noise-added patterns in the learning stage. Owing to a volatile property of atomic switches, added noises of displayed patterns are not stored in the neural network. As a result, we revealed the "noise removal" function or "robustness" of atomic switches in pattern recognition. We do not have to use noiseless clean images practically to learn (store) patterns. This model can also be applied to detecting moving objects in moving image processing.



Fig. 2. Demonstration of pattern recognition by the Hopfield-type neural network using atomic switches.

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## Superconductivity as a Platform for Novel Functionality

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#### 1. Outline of Research

While BCS theory explains successfully at microscopic level the phenomenon of superconductivity and is definitely a pyramid in physics, it is not the end of endeavor for understanding superconductivity. Nambu noticed that the success of BCS theory violating electron-number conservation implies the broken local gauge symmetry. This notion turns out very important which is linked to the Ginzburg-Landau theory where phase of superconductivity order parameter was put intuitively and pushed forward by Abrikosov, leading to the discovery of quantum vortex. The importance of phase of superconductivity gap function is best appreciated in the tunneling phenomenon between two superconductors across a thin insulator as was discovered by Josephson.

In MANA we have been devoting continuous efforts to exploration of new facets of superconductivity. Stimulated by an experimental breakthrough, we discovered a  $\pi$ -kink state of phase dynamics in nano Josephson junctions built in cuprate high-Tc superconductor BSCCO-2212, where the phase twists work as nano windmills to pump large dc energy into cavity resonance and radiation of THz electromagnetic wave. We also conceived a SQUID-like structure formed by two nano superconductor needles, which can generate and measure nonlocal spin entanglement between two electrons splitted from a Cooper pair. Recently we designed nano devices made of topological superconductors to braid the charge-neutral Majorana bound states (MBSs) in terms of local gate voltages, which realizes the non-Abelian statistics expected to be useful for decoherence-free quantum computation and topological single-electron pumping.<sup>1)</sup>

#### 2. Research Activities

#### (1) Novel properties of TRSB superconductivity.<sup>2,3)</sup>

As one example of our efforts along the line described above, we introduce here in some detail our recent works on superconductivity with three or more bands, where a state with broken time-reversal symmetry (TRS) is stabilized by repulsive inter-band coupling at zero magnetic field. In a Josephson junction between a three-band superconductor with broken TRS and a single-band superconductor shown in Fig. 1, as a consequence of the broken TRS, critical currents



Fig. 1. Schematics for Josephson junction between a single-band superconductor and a three-band TRSB one. Arrows represent phases of superconductivity order parameters.

in two opposite directions are unequal,<sup>2)</sup> which was observed in an early experiment based on Josephson junctions made of conventional and iron-based superconductors. Our theory on the novel TRSB superconductivity combined with the experiment will nail down a novel superconducting state, and thus cut a new fascinating facet of iron-based superconductivity. We also predict an unconventional state characterized by clustering vortices in specific regime of material parameters when the TRSB superconductor is exposed to magnetic field.<sup>3)</sup>



- Fig. 2. Top: STM images of zero-bias conductance around vortices trapped at atomic steps with brightness standing for DOS of zero-energy quasiparticle excitations; Bottom: order parameter, supercurrent and DOS of zero-energy quasiparticle excitations around a Josephson vortex derived by on BdG equation.
- (2) Josephson vortex in one-atomic-thin superconductor.<sup>4,5)</sup>

Superconductivity in two dimensions as evidenced by existence of quantized vortices came up as a surprise a couple of years ago since it was believed that thermal fluctuations would destroy the long-range order. A successful measurement on supercurrent by a MANA team made it undoubtable probably in the best way since the Meissner effect is not available due to imperfect screening of magnetic field in mono-atomic thick systems. Based on the state-ofart STM/STS technique and theoretical analysis in terms of Bogoliubov-de Gennes equation, our joint team of MANA, University of Tokyo and JAEA discovered recently that Josephson vortices are realized at atomic steps of In monoatomic layer on silicon [111] surface (Fig. 2).<sup>4,5)</sup> This indicates that atomic steps between In terraces of In layer work as tiny Josephson junctions, which are mass produced, self assembled and easy manipulated. This research reveals a promising platform for future quantum devices.

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## Surface Atomic Scale Logic Gate

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#### 1. Outline of Research

The Pico-Lab CEMES-CNRS Toulouse MANA satellite is working on experimental and theory for the design of QHC logic gates, their current drive and mechanical input interconnects and on the exploration of the atomic scale logic gate complexity roadmap to master the emergence of a maximum quantum computing power inside a single molecule or a surface atomic scale circuit.

#### 2. Research Activities

#### (1) Setting up the LT-UHV – 4 STM & UHV SEM.

The Toulouse MANA satellite has now received and installed its LT-UHV 4 STM & UHV SEM equipment for atomic scale contact experiments on a DB logic gate circuit, on a single molecule logic gate and more generally to study single molecule-machines. Each of the four LT-UHV-STM has a stability of 2 pm and is able to manipulate atoms one by one independently and on the same surface.

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

Using acetophenone molecule mechanical inputs on a Si(100)H surface, the first ever-complete dangling bond (DB) QHC AND gate (Fig. 1) was designed. Using the K-ESQC theory, I-V characteristics were calculated and the molecule latch conformation optimized using ASED+ completed by a detail analysis of the latching reaction path on the ground state potential energy surface of the system using an NEB algorithm. The experimental construction of this DB gate on Si(100)H was prepared by analyzing in detail the STM imaging conditions of the Si(100)H surface dimer rows showing an apparent 1/2 surface lattice lateral shift inducing a wrong surface localization of the H atoms to be extracted for constructing the DB logic gates.<sup>1)</sup> At the origin of the functioning of QHC gates, electronic interference effects were re-visited using our new CI-ESQC theory to include many-body effects.<sup>2)</sup>



Fig. 1. Surface configuration of the DB QHC AND logic gate on Si(100)H with its 2 acetophenone molecule latch inputs. The calculated I-V curves are demonstrating a nice Boolean AND response.

#### (3) Design of molecule QHC logic gate.

QHC molecule logic gates design have been pursued to explore how the above molecular latching can be embedded in a single molecule. A derivative of the coronene was first used with agressive nitro groups as molecular latchs inputs (Fig. 2). One nitro rotation leads to a ground state shift up by 0.5 eV and 0.8 eV for two as compared to a "0" logical input perpendicular nitro conformation.  $\Pi$ -electronics system lateral extensions were attempted using for example a circumcorronene core equipped with 3 diazobenzene switchable latchs (Fig. 2). The ON trans conformation of each latch is only inducing step-by-step a 0.1 eV up shift in energy of the ground state of the molecule as compared to the OFF cis conformation.



Fig. 2. Two molecules equipped with their input chemical groups. The corronene derivative with its nitro latches (left) is showing a nice adder functioning and not the 3-diazobenzene-circumcorronene (right).

#### (4) Mechanical inputs.

For an atomic scale logic gate, the advantage of mechanical inputs is the very fast input response time. We have explored theoretically the driving power of an inelastic tunneling current able to switch a molecule-latch or to drive a molecule-motor.<sup>3)</sup> Our model is using the ground and excited states of the molecule-latch and a semi-classical equation of motion driven by the tunneling shot noise.<sup>3)</sup> Experimentally, we have explored the limit of solid-state nanogears miniaturization reaching 35 nm in diameter, 15 nm in thickness for 6 teeth SiO<sub>2</sub> nanogears.<sup>4)</sup> They were AFM manipulated along a 3 nm step height on a graphite surface to demonstrate the potential gearing effect between a 3 nm molecular object and a 15 nm in height solid state nanogear (Fig. 3). Mechanical gearing can be one effect to control the molecule latch input (Fig. 1).



Fig. 3. A sequence of tapping mode AFM images of a single nano-gear rotation along a 3 nm height step. The AFM tip manipulates the nanogear by step of 30 nm with about 1/12 of a turn each time.<sup>4</sup>

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## Integration of Nano Functionality for Novel Nanosystems MANA Principal Investigator Tomonobu NAKAYAMA

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1. Outline of Research

We develop novel techniques and methodologies toward the realization of novel nanosystems for future information technology. Development and application of multiple-probe scanning probe microscopes (MP-SPMs) and fundamental researches on molecular manipulations, low-dimensional nanostructures and neuromorphic networks, are explored. These are aiming at a realization of functional nanosystems which transmit and transduce electrical, optical, mechanical, ionic and magnetic signals.

#### 2. Research Activities

#### (1) Multiple-probe Scanning Probe Microscopes.<sup>1-3)</sup>

MP-SPM has simultaneously and independently controlled 2 to 4 scanning probes<sup>1)</sup> which are brought into electrical contact to a single nanostructure and reveals its electrical property.<sup>2)</sup> Implementation of Kelvin-probe force microscopy (KPFM) mode in our MP-SPM realized non-contact observation of potential distribution over a nanosystem under a current bias. As an alternative non-contact MP-SPM operation, eddy-current damping microscopy (ECDM) mode was successfully introduced, where an eddy-current induced damping of an oscillating magnetic probe was detected to obtain a conductance distribution over the nanosystem.<sup>3)</sup>

The above non-contact electrical measurement modes in our MP-SPM measurements will provide novel methodologies for nanosystem characterization. Examples of KPFM and ECDM images are shown in Fig. 1.



Fig. 1. Images of graphene on SiO<sub>2</sub> using two different modes for noncontact electrical property measurements implemented in our MP-SPM; Eddy-Current Damping Microscopy (ECDM) and Kelvin-Probe Force Microscopy (KPFM) modes.

# (2) Fabrication of functional nanostructures and nanomaterials.<sup>4-7)</sup>

Creating functional nanostructures and nanomaterials, followed by measurements of their physical properties, is an important part of our research towards a realization of functional nanosystems. We are currently working on surface superconductivity for quantum computing and neuromorphic



Fig. 2. (a) An STM image of Si(111)- $(\sqrt{7}x\sqrt{3})$ -In and (b)-(d) zero bias conductance (dI/dV) images of the same area as (a) under different magnetic fields. Bright features in (b)-(d) correspond to trapped vortices.

networks for massively parallel analog computing (braintype computing).

It was clearly shown that the atomic steps on the Si(111)- $(\sqrt{7'}\sqrt{3})$ -In superconducting surface<sup>4)</sup> provide Josephson junctions.<sup>5)</sup> Vortices trapped at the atomic steps were directly imaged by low-temperature STM under controlled magnetic field (Fig. 2) and their shapes were in detail analyzed by theoretical calculations. This work was done in collaboration with Prof. Y. Hasegawa of ISSP, Univ. of Tokyo and with Dr. X. Hu of MANA.

For realizing neuromorphic networks, we designed a peptide (GFPFRAGFP) molecule and self-assembled the molecules into one-dimensional nanofibers under an aqueous condition. The high density of aromatic rings involved in GFPFRAGFP enhanced the conductance even in a vacuum condition.<sup>60</sup> Another fibrous structure was made of doped-polyaniline (PANI). In both cases, thanks to their flexibility, complex networks which have many nodes and linkages could be formed. In our preliminary measurements using MP-SPM, both GFPFRAGFP and PANI networks often showed non-linear I-V characteristics as a whole network and hysteresis response to transient voltage application.

We also demonstrated a chemical soldering between a radical front-end of poly-diacetylene wire and a single  $C_{60}$  molecule.<sup>7)</sup>

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## Mesoscopic Superconductivity and Quantum Information Physics

MANA Principal Investigator (Satellite at Tokyo Univ. Sci., Japan) Hideaki TAKAYANAGI

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#### 1. Outline of Research

MANA Research Associate

Guest Researcher Graduate Student

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.



Fig. 1.  $I_c$  and  $R_n$  normalized by those values measured without illumination as a function of *P*.

#### 2. Research Activities

# (1) Optical effect on proximity-induced superconductivity in graphene.

We studied optical effects on proximity-induced superconductivity in graphene by illuminating superconductor/ graphene/superconductor junction with light at the wavelength  $\lambda = 1.31 \mu m$ . At T = 40 mK, supercurrent flowing through the graphene channel is observed and the critical current ( $I_c$ ) monotonically decreases with increasing illumination power (P) though normal state resistance does not change (Fig. 1). This reduction in  $I_c$  originates from suppression of proximityinduced superconductivity in graphene by optical irradiation. Reduction rate of  $I_c$  is weakly dependent on gate voltage applied to graphene (Fig. 2). This indicates that suppression of superconducting state can be attributed to at least two factors: direct breaking of Cooper pairs by the absorption of photons and heating of electron temperature through energy relaxation of hot carriers. Our results will pave a new path to connect superconductivity and optoelectronics.



Fig. 2. Irradiation power dependence of  $I_c / I_c^{dark}$  vs  $V_g$ . Solid lines are linear fit representing dependency of  $I_c / I_c^{dark}$  on  $V_g$ .

# (2) Transport property of a Self-assembled mesoscopic superconducting ring.

We suggest a possibility of making a dc-SQUID using phase-slip centers (PSCs) in a mesoscopic superconducting ring. Self-assembled nanometer-scale quantum rings were fabricated by droplet epitaxy. Differential resistance as a function of current *I* and magnetic field *B* is shown in Fig. 3. The voltage develops in step-like increments from almost zero voltage at critical current  $I_{cl}$ . Voltage steps from a resistive branch to other higher resistivity branch were observed at  $I_{c2}$ ,  $I_{c3}$  and  $I_{c4}$ . These voltage steps indicate the formation of spatially localized voltage centers (VCs) including PSCs in superconducting quasi one dimensional superconductors. Observation of periodic quantum oscillations of  $I_{c3}$  with a period of 0.28 T determined by the area of the ring indicates successfully making a dc-SQUID using PSCs in a mesoscopic superconducting ring.



Fig. 3. Differential resistance as a function of *I* and *B*.

## **Electrostatically Reversible Polarity Switching in** Ambipolar $\alpha$ -MoTe<sub>2</sub> Transistors MANA Principal Investigator

MANA Researcher

Kazuhito TSUKAGOSHI Shu Nakaharai



#### 1. Outline of Research

A doping-free transistor made of ambipolar  $\alpha$ -phase molybdenum ditelluride ( $\alpha$ -MoTe<sub>2</sub>) is proposed in which the transistor polarity (p-type and n-type) is electrostatically controlled by dual top gates. The transistor has a pair of top gates. The voltage signal in one of the gates determines the transistor polarity, while the other gate modulates the drain current. We demonstrate the transistor operation experimentally, with electrostatically controlled polarity of both p- and n-type in a single transistor.

#### 2. Research Activities

In order to apply transition metal dichalcogenides (TMDCs) to CMOS (complementary metal oxide semiconductor) circuits, the transistor polarity must be controlled to be both positive (p) and negative (n) type. However, polarity control of transistors is generally difficult in TMDCs because of the large Schottky barrier at the metal-semiconductor junction, which is fixed, irrespective of the metal species, by the Fermi-level pinning effect. In the case of MoS<sub>2</sub>, for example, which has been explored most actively among the TMDC family, the transistor polarity is mostly only n-type. In WSe<sub>2</sub>, the transistor polarity could be ambipolar owing to the comparable barrier heights for electrons and holes, while both of the barriers are so high that the suppressed carrier injection reduces the drive current of transistors for both p- and n-FETs. One possible solution for these carrier injection issues in TMDCs could be the formation of electric double-layer gates by using ionic liquids. In this case, an extremely large gate capacitance allows both p- and n-type conduction by thinning the Schottky barrier to enhance the tunneling of electrons and holes.

Flakes of  $\alpha$ -MoTe<sub>2</sub> were exfoliated by sticky tape from bulk crystals of  $\alpha$ -MoTe<sub>2</sub>, which were grown by the chemical vapor transport method. The ambipolar behavior of an  $\alpha$ -MoTe<sub>2</sub> transistor is obtained.<sup>1)</sup>

Local electrostatic control of the transistor polarity was achieved in transistors with two top gates in series on an  $\alpha$ -MoTe<sub>2</sub> channel<sup>2</sup> (Figs. 1a, b). These two top gates were biased independently, and the back gate was grounded (Figs. 1c, d). The polarity of the bias of one of the two gates determines the polarity of the transistor in response to the sweeping of the other top gate (Figs. 1e, f). The transistor operations in p- and n-FET modes represent electrostatical reversible polarity switching in an ambipolar α-MoTe<sub>2</sub>.

Polarity controllability allows us to realize a highly flexible design for logic circuits, leading to highly efficient logic operations. This result paves the way to advanced electronic devices based on atomically thin semiconductors



Fig. 1. (a) An optical micrograph of a dual top gate transistor. The broken line shows the region of the α-MoTe<sub>2</sub> flake. (b) A schematic of the transistor structure. The gap between the two top gates was 100 nm. (c) The band configurations of on and off states in the p-FET mode at source side top-gate voltage  $V_{tgS}$  < 0. The on state occurred at drain side top-gate voltage  $V_{top} < 0$ , and the off state at  $V_{tgD} > 0$ . (d) The band configurations of on and off states in the n-FET mode at  $V_{tgS} > 0$ . The on and off states were given by  $V_{tgD} > 0$  and  $V_{tgD} < 0$ , respectively. (e) Experimental results for on/off operation in the p-FET mode  $(V_{tgs} = -5 \text{ V})$ . The inset is a logarithmic plot. (f) Experimental results of an on/off operation in the n-FET mode ( $V_{tg8} = 5$  V), with a logarithmic plot provided in the inset.

with reduced power consumption.

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## Nanoarchitectonics of Hybrid Artificial Photosynthetic

### System

MANA Principal Investigator

(Field Coordinator) MANA Research Associate Graduate Student Jinhua YE

L. Liu, Q. Kang, K. Chang X. Meng, G. Liu, M Li, Q. Yu, L. Shi



#### 1. Outline of Research

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



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

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

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

2) Nanoarchitectonics of the photosynthesis system will be conducted, by not only fabrication of nano particles using various soft chemical method, but also assembling of nano-



Fig. 2. Left: Image of the photothermal CO<sub>2</sub> conversion over Group VIII nanometals. Right: CO<sub>2</sub> conversion to CH<sub>4</sub> on Ni/Al<sub>2</sub>O<sub>3</sub> catalysts.<sup>1)</sup>

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.

#### 2. Research Activities

(1) Highly efficient solar fuel production by utilizing photothermal effect over Group VIII nanocatalysts.<sup>1)</sup>

Inspired by the rapidly developed surface plasmon resonance (SPR) of metal nanomaterials, we have recently succeeded in achieving efficient solar fuel production over VIII group nanocatalysts, which reaches 6 orders of magnitude higher than that of the present photocatalysis method, approaching the level of practical application. The highly efficient  $CO_2$  conversion to  $CH_4$  fuel is attributed to the comprehensive characteristics rendered by VIII group nanocatalysts, including effective energy utilization to the whole range of solar spectrum, excellent photothermal performance, and unique activation ability (Fig. 2). It is proposed that the overall water-based  $CO_2$  conversion process can be achieved by combining light-driven  $H_2$  production from water and photothermal  $CO_2$  conversion with  $H_2$  in future.

(2) Exploiting noble-metal-free cocatalysts for efficient H<sub>2</sub> evolution from solar water splitting.<sup>2)</sup>

We have successfully developed a composite material consisting of CdS nanocrystals grown on the surface of a nanosized  $MoS_2$ /graphene hybrid as a high-performance noble-metal-free photocatalyst for H<sub>2</sub> evolution under visible light irradiation. The  $MoS_2$ /G composite cocatalysts showed even higher activity and stability than the well-known Pt in lactic acid solution (Fig. 3). The new composite photocatalyst is expected to have great potential as a promising photocatalyst with high efficiency and low cost for photocatalytic H<sub>2</sub> evolution production.



Fig. 3. Left: HRTEM images of the MoS<sub>2</sub>/G-CdS composite photocatalyst. Right: Cycling test for photocatalytic H<sub>2</sub> evolution,  $\lambda > 420$  nm.<sup>2)</sup>

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## Solid-State Batteries

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



#### 1. Outline of Research

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

#### 2. Research Activities

#### (1) Sol-gel synthesis of LiCoO<sub>2</sub> epitaxial films.<sup>1)</sup>

Battery performance is governed not only by bulk properties of the battery materials but also by their interfaces. For example, grain boundaries are often highly-resistive and thus lowers the battery performance. Although epitaxial growth is anticipated to remove such grain boundaries, physical deposition processes, which are usually used in epitaxial growth, do not fit mass production. Therefore, we have developed a wet process for the epitaxial growth.

In this study,  $LiCoO_2$ , which is a typical cathode material in current lithium-ion batteries, is formed into thin films by a sol-gel method. An aqueous solution of precursors is coated on single-crystal substrates by a spin-coating method. By optimizing the heat treatment condition, we have succeeded in the epitaxial growth of the  $LiCoO_2$  films. Crystal orientation is controllable by selecting different crystal faces of SrTiO<sub>3</sub> as the substrates, as demonstrated in Fig. 1.

#### (2) Silicon anodes in solid-state system.<sup>2)</sup>

Lithium-silicon alloys are regarded as anode materials with the greatest potential because of the high theoretical capacity more than then times higher than that of graphite, low electrode potential, and high abundance. However, the alloy electrodes exhibit a large volume change upon the electrode reactions, which causes some drawbacks. For example, electrode potential of anodes is usually out of the electrochemical windows of organic electrolytes, even in the case of graphite anode in lithium-ion batteries. Of course, the electrolyte is reductively decomposed at the anode surface; however, the decomposition products covering the surface protect the electrolyte against further decomposition. On the other hand, repetitive expansion/shrinkage during the battery operation in Si anodes gives recurrent appearance of new surface, where the decomposition continues and results in the degradation of anode performance. In this study, electrode properties of Li-Si alloys were investigated in a solid electrolyte, 70Li<sub>2</sub>S–30P<sub>2</sub>S<sub>5</sub> glass ceramic.

The Si–FeS formed into films by pulsed laser deposition exhibits high performance in the solid electrolyte, as demonstrated in Fig. 2. The rate capability is quite high: the anode delivers a high discharge capacity of 2000 mAh  $g^{-1}$  even at an extremely high discharge rate of 100 C, when the anode is thin (30 nm). Moreover, the Si–FeS anode retains the high rate capability, even when it is bulky.



Fig. 1. X-ray pole figures for 003 reflections from  $LiCoO_2$  films grown on  $SrTiO_3$  (111) (a), (110) (b), and (100) (c) substrates, and a cross-sectional TEM image of a film grown on  $SrTiO_3$  (100) substrate (d).



Fig. 2. Discharge curves of Si–FeS films with thickness of 30 and 1000 nm at various discharge rates.

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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 MANA Research Associate Hidenori Noguchi

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#### 1. Outline of Research

Graduate Student

One of the most challenging tasks for chemists/ material scientists is the construction of efficient conversion systems of energy and materials. We are trying to establish techniques to construct interfacial phases for highly efficient conversion of energy and materials, mainly at solid/liquid interfaces, by arranging metal, semiconductor, organic molecules, and nanomaterials 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 are working on 1) construction of catalytic interfaces by arranging atoms on metal surfaces in ordered manner, 2) construction of functional 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 electrocatalysts is the key to achieve sustainable society because of their central role in interfacial energy conversion such as fuel cell. Oxygen reduction reaction (ORR) is one of the most important processes in fuel cells. Although Pt based materials are currently the most efficient electrocatalyst for ORR, they have several problems such as high cost, less abundance, poor stability, and still sluggish kinetics and there are many efforts to find alternative catalysts. Recently we showed theoretically that boron nitride monolayer, which is obtained by substituting all carbon atoms in graphene by B and N atoms, can be used as an ORR catalyst, although it is an insulator.<sup>1)</sup> DFT calculations for BN/Au(111) show a slight protrusion of the unoccupied BN states towards the Fermi level due to the interaction between BN and Au(111) and presence of a metastable highly activated configuration of O<sub>2</sub> on h-BN/ Au(111) and stable configurations of O<sub>2</sub> adsorbed at the edge of the BN islands on Au(111) surface, showing the possible ORR activity of BN/Au(111).<sup>2)</sup> Electrocatalytic activities of various types of h-BN, *i.e.*, spin coated BN nanotube (BNNT) and BN nanosheet (BNNS) and sputter deposited BN, on Au

electrodes as well as those of BNNS modified glassy carbon (GC) and Pt electrodes for oxygen reduction reaction (ORR) were examined to prove the theoretical prediction. The overpotential for ORR at Au electrode was reduced in all cases, proving the theoretical prediction.<sup>2,3)</sup> The highest activity was obtained by the BNNS



Fig. 1. Current-potential relations at various electrodes in  $\mathbf{O}_2$ saturated H<sub>2</sub>SO<sub>4</sub>.

modification possibly due to the presence of B-and/or N-edge structures. While the BNNS modification was very effective to improve ORR activity at Au electrode, it has no and negative effects at glassy carbon (GC) and Pt electrodes, respectively, as shown in Fig. 1, confirming the important role of BN-Au interaction for ORR activity enhancement. ORR activity of BNNS/Au is still far from practical as it is much less active than Pt and produces not water by 4-electron process but H<sub>2</sub>O<sub>2</sub> by 2-electron process. We are currently working to improve the efficiency by increasing the BN-Au interaction.

(2) Construction of Functional Interfaces by Forming Ordered Molecular Layers on Metal and Semiconductor Surfaces.

Construction of metal-organic monolayer-metal (M-OM-M) and metal-organic monolayer-semi- conductor (M-OM-S) junctions has attracted much attention because of their potential applications in next generation electronic devices. We have developed a novel method to construct a metal-organic monolayer- semiconductor (M-OM-S) junction on a hydrogenterminated n-type Si(111). The junction can be formed by sequential surface reactions of 1)

formation of an organic monolayer with thiol terminal group, 2) platinum deposition onto the thiol group via adsorption of a platinum complex followed by chemical reduction, and finally 3) continuous Ag layer formation by electroless deposition. This interface exhibit rectifying behavior as shown in Fig. 2.4



(3) 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. This year we have successfully monitored the potential induced structure changes such as surface reconstruction lifting, adsorption of oxygen species, formation of surface oxide bilayer, reduction of surface oxide, and surface reconstruction of Au(111) and Au(100) in H<sub>2</sub>SO<sub>4</sub> solution by surface x-ray scattering (SXS) in situ in real time,<sup>5)</sup> and clarified the effects of atomic geometry and electronic structure of Pt surfaces on molecular adsorbates based on the SERS spectra measured on Pt of various crystal orientation and on Pt-epitaxial monolayers, respectively.<sup>6)</sup> References

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## **Reticular** Materials

MANA Principal Investigator MANA Scientist MANA Research Associate **Omar M. YAGHI** Kentaro Tashiro Kappam V. Sajna, Pradip Sukul



#### 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, sequence, as well as three dimensional orientation of metal centers (Fig. 1).<sup>1–5)</sup> Fig. 1 shows a representative molecular structure of the hetronuclear multimetallic species only accessible by our approaches.<sup>5)</sup>



Fig. 1. Molecular structure of a hetronuclear multimetallic species containing site-specifically located four types of eight metal centers in a well-defined H-shaped topology.

#### 2. Research Activities

# (1) Self-Assembling Behaviors of Water-Soluble MOCAs in Aqueous Media.<sup>6</sup>

By putting water-soluble functionalities into the molecular structure of Metal–Organic Complex Arrays (MOCAs), we successfully synthesized water-soluble version of MOCAs (WSMOCAs). When a WAMOCA containing three different metal centers was dissolved in aqueous media, it was molecularly dispersed under neutral pH conditions, while upon lowering the pH value into acidic conditions it self-assembled to give hollow spherical objects, as visualized by microscopic observations.

#### (2) Self-Assembling Behaviors of Diphenylalanine-Based Metal Complex Arrays.<sup>7</sup>

Diphenylalanine is a well-known structural motif for the design of peptide derivatives that self-assemble into particular nanostructures such as fibers, tubes, and so on. We newly synthesized a diphenylalanine derivative that possesses multiple terpyridine ligands at the side residues. Scanning electron microsopy revealed that this nonmetallated species self-assembled into um-lengthed fibers with a uniform width of 10 nm (Fig. 2). Metallation at the terpyidine ligand moieties affects on the self-assembling behaviors of the peptide, where a Re(I) metallated compound retains the fiber-forming capability, while a Pt(II) metallated analogue fails to afford any similar structures. Of interest, when either of the two terpyidine ligands in the structure was site-selectively metallated with Pt(II) to give two isomers, the self-assembling behaviors of these two singly metallated species were contrasting, as only one of the isomer was able to form fibrous assemblies.



Fig. 2. SEM image of fibrous assemblies of a non-metallated diphenylalanine-based peptide bearing multiple terpyridine ligands at the side residues.

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## Dye-Sensitized Solar Cells and Core-Shell Nanowires

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



#### 1. Outline of Research

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

We 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 both the MANA UCL post-doc and the MANA UCL student, as well as visits to UCL from researchers in NIMS.

#### 2. Research Activities

#### (1) Atomic and Electronic Structure of Dye Molecules on *TiO*<sub>2</sub>.

We have finalized our modelling of  $TiO_2$  and dyes on  $TiO_2$ . We studied Al doping in  $TiO_2$  (which is known experimentally to alleviate the bad effects of oxygen vacancies), considering the effect on dye binding and electronic structure on  $TiO_2$ .<sup>1)</sup> We found that Al compensates for the oxygen vacancies, removing the band-gap states that degrade performance. We also modeled the diffusion of oxygen vacancies, shown in Fig. 1, and showed that they would move to combine with the dopants. We have also investigated the effect of varying the acid binding group to substrates, both in terms of binding strength and resulting electronic structure<sup>2</sup> to optimize the binding motif. We found that a careful choice of the acid (not necessarily carboxylic acid) for each surface will improve device performance.



Fig. 1. Diffusion of an oxygen vacancy in  ${\rm TiO}_2$  showing pathway taken to bind to Al dopants.

#### (2) Properties of Semiconductor Nanostructures.

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 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 also applying the CONQUEST code to study the three-dimensional structures, hut clusters, that form when Ge is deposited on Si(001), in close collaboration with Dr. T. Miyazaki of the CMSC. Fig. 2 shows details of our modelling of the growth of one of these "hut" clusters.<sup>3)</sup> We also study the surfaces of nanostructures, including diffusion of hydrogen,<sup>4)</sup> which is important during growth of nanowires and nanostructures.



Fig. 2. Top: Model of Ge hut cluster on Si(001) showing new facets growing (yellow). Bottom: Detail of end facet, showing dimer locations (new dimers shown in yellow).

#### (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, and to use up to 25% of the Japanese K computer with nearperfect scaling. We are also continuing to develop novel approaches to extend the functionality of CONQUEST: recently we have demonstrated the first linear scaling molecular dynamics<sup>5)</sup> (on over 32,000 atoms), as well as new methods to perform efficient, large-scale calculations.<sup>6)</sup>

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## Smart Nano-Biomaterials

MANA Principal Investigator (Field Coordinator) MANA Scientist NIMS Junior Takao AOYAGI

Mitsuhiro Ebara Qinghui Shou



Near-infrared (NIR) light-responsive shape-memory films were prepared through the photo-initiated crosslinking reaction of  $poly(\epsilon$ -caprolactone) (PCL) macromonomers with acryloyl terminal groups in the presence of gold nanorods (AuNRs). To incorporate the AuNRs homogenously within the films, the surfaces of AuNRs were modified with PCL via surface-initiated ringopening polymerization (SI-ROP), taking into the consideration of both miscibility. The shape-switching temperature of PCL was adjusted in the physiological temperature range by controlling the melting temperature of PCL. Exposure to NIR light successfully induced the photothermal heating of embedded AuNRs and, consequently, the shape-switching transition. After NIR irradiation at higherpower densities, the film completely recovered its original shape. When exposed to lower-power densities, a local temperature increase was observed in the area where the beam hit. Therefore, local shape memory transformations were obtained. These results show the potential of AuNRs -embedded PCL films as spatially controllable, shapememory materials that actuate in physiologically relevant temperature ranges and from remote stimuli.<sup>1)</sup>

#### 2. Research Activities

Preparative schemes of the AuNR-embedded PCL film are summarized in Fig. 1. First AuNRs with different sizes were synthesized using seed-mediated method. The condition for absorbtion/desorption of CTAB from the surface of AuNRs was investigated. After twice centrafugation of AuNRs (CAuNR=0.13 mmol·L<sup>-1</sup>), the fully removing of CTAB could be realized with



Fig. 1. Fabrication of AuNRs-PCL composite film. (a)Synthesise of PCL-modified AuNRs via surface- initiated ring opening polymerization. (b) Preparation of AuNR-embedded PCL films through crosslinking of two- and four-branch PCL macromonomers in the presence of PCL-modified AuNRs.



VAuNRs:VDMSO=0.5:0.5-0.7:0.3. And then the surface of AuNRs was modified with PCL through SI-ROP. NIR light-responsive shape memory films were successfully prepared through crosslinking of PCL macromonomers in the presence of AuNRs. This enabled to incorporate AuNRs into PCL film uniformly without hindering the crystallization of PCL. The shape-switching temperature was adjusted in physiological temperature range by controlling the melting temperature of PCL.

Exposure to NIR light could successfully induce the photo-thermal heating of embedded AuNRs and consequently, shape-switching transition (Fig. 2). Upon NIR irradiation, the film completely recovered its original shape. Local shape-memory transformation was also obtained when the limited area was exposed to the light. The NIR irradiation was used to control cell morphology. Cell alignment in the NIR-irradiated region was lost and random cell migration was ensured because it caused the surface transition to a flat surface, while cells on the non-illuminated region were still aligned along the direction of the temporal pattern. This finding is novel in that it is the first study that controls the cell orientation locally and remotely on the shape-memory nano-patterns by NIR light irradiation. Therefore, we believe that NIR-responsive shape-memory system offers significant promise for the creation of topographically tunable substrates because of their remotecapability to undergo large elastic deformations and to rapidly return to their initial state.



Fig. 2. Images of the NIR light-induced shape transitions PCL films (a) without AuNRs (b) with 0.4 wt% AuNRs, intensity 0.4 W cm<sup>2</sup> and (c) with 0.4 wt% AuNRs, intensity 0.8 W cm<sup>2</sup>.

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## Creation of Nanostructured Scaffolds Using Single-Walled Carbon Nanotubes and Their Cellular Effects MANA Principal Investigator Guoping CHEN

MANA Scientist NIMS Junior Researcher Naoki Kawazoe Hongli Mao



#### 1. Outline of Research

The unique properties of nanomaterials offer excellent platforms for biomedical applications. Since cells in biological systems create and directly interact with nanostructured extracellular matrices (ECM), nanomaterials with excellent biomimetic features and physiochemical properties show great potential in the fabrication of novel biomaterials and scaffolds for tissue engineering. Among various nanomaterials, carbon nanotubes (CNTs), especially single-walled carbon nanotubes (SWCNTs) have attracted intense interest and shown promising applications in the realm of targeted drug/gene delivery, diagnostics, cancer research and tissue engineering. The success of nanomaterials-based applications in disease diagnosis and therapy largely depends on whether the designed nanomaterials can be easily internalized by cells. However, the internalized nanomaterials may produce some negative effects on cells. Therefore, one of the crucial issues regarding nanomaterials-based applications that have to be addressed is to understand how nanomaterials interact with cells and to uncover their potential risks.

In this study, SWCNTs were incorporated in 3D scaffolds by modifying SWCNTs with biological molecules and then being hybridized with collagen hydrogels and porous sponges. Their interactions with cells, especially the cellular uptake and the associated cellular effects were investigated in 2D and 3D cell culture systems.

#### 2. Research Activities

SWCNTs were functionalized with collagen (collagen– SWCNTs). The collagen–SWCNTs retained the inherent properties of SWCNTs and the suspension solution was stable for months. The cellular effects, uptake and intracellular distribution of the collagen–SWCNTs were investigated by using them for 2D culture of bovine articular chondrocytes (BACs). The collagen–SWCNTs showed no obvious negative cellular effects and high amount of SWCNTs were internalized by cells. The internalized collagen–SWCNTs were distributed in the perinuclear region and retained in the cells for more than one week. Adsorption of SWCNTs by ECM was shown to be an important step for cellular uptake of SWCNTs. The results suggested that SWCNTs functionalized by collagen should be suitable for applications in biomedicine and biotechnology. The Col-SWCNTs were also used as imaging probes for labeling of human mesenchymal stem cells (hMSCs) and the inherent Raman scattering of SWCNTs was used to image the SWCNT-labeled cells. The results showed that the Col-SWCNTs exhibited efficient cellular internalization by hMSCs without affecting their proliferation and differentiation. The prolonged dwell time of Col-SWCNTs in cells ensured the long-term labeling for up to 2 weeks. The good cytocompatibility and long dwell time of Col-SWCNTs revealed the potential of SWCNTbased long-term stem cell labeling.<sup>1)</sup>

Furthermore, SWCNTs were incorporated in collagen hydrogels and collagen porous sponges to construct 3D cell culture system to investigate 3D interaction between SWCNTs and cells. The SWCNTs/Col hydrogels showed no negative effects on the viability of BACs. Uptake of SWCNTs by BACs was confirmed by using UV-vis-NIR spectroscopy and confocal Raman imaging. The internalized SWCNTs were prevalently accumulated in the perinuclear region. The results indicated that SWCNTs could be internalized by cells when being cultured in the 3D biomimetic collagen hydrogels.<sup>2)</sup> 3D porous collagen sponges incorporated with SWCNTs (hybrid porous sponges) were prepared by using ice particulates as a porogen material and coating with SWCNTs. When BACs were cultured in the hybrid sponges, the cells adhered and spatially distributed in the hybrid porous sponges. The incorporation of SWCNTs in the collagen porous sponges promoted cell proliferation and production of sulfated glycosaminoglycans (sGAG). Confocal Raman imaging revealed that SWCNTs could be internalized by cells. The hybrid porous sponges not only provided nanostructured pore surfaces to facilitate cell proliferation and ECM secretion but also supplied nanomaterials for cellular uptake which may be useful for delivery of bioactive molecules into cells.<sup>3)</sup> Due to similarity of 3D culture in the hybrid porous sponges to the in vivo nano- and microenvironment, the results reflected the responses of cells to the SWCNTs more realistically than 2D culture. The hybrid scaffolds should be useful for tissue engineering.

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## Nanotherapeutics Based on Redox Polymer Nanoarchitectonics

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Yutaka Ikeda Yukichi Horiguchi, Toru Yoshitomi



#### 1. Outline of Research

The objective of our research is to create new bioactive materials for high performance therapeutic system. In order to use materials in vivo, interactions between materials surface and bio-components such as blood and tissue must be controlled. Non-biofouling surface is one of the most important characters for high performance biomaterials design. Using our surface constructing technique thus developed, we have developed novel bionanoparticles, which scavenge excessively generated reactive oxygen species (ROS). Using our new nanoparticle (redox nanoparticle, RNP), we have developed novel nanotherapeutic system. In 2014, we have developed nanotherapeutic system for a colitis associated colon cancer (CAC). We have also developed injectable gels, which scavenge ROS. We have applied it for periodontal disease and anti-adhesive materials.

#### 2. Research Activities

(1) Preparation of redox nanoparticles (RNP) and application for colitis associated colon cancer (CAC).

The mucosa of colitis-associated colon cancer (CAC) exhibits overproduction of reactive oxygen species (ROS), which increase cancer cell resistance to conventional chemotherapy such as irinotecan (Iri). In addition, high dose of Iri administration cause severe adverse effects including diarrhea and intestinal inflammation. In previous study, we developed a redox nanoparticle (RNP<sup>o</sup>) prepared by self-assembly of an amphiphilic block copolymer possessing stable nitroxide radical TEMPO, an ROS scavenger, as a side chain of hydrophobic segment (Fig. 1). The orally administered RNP<sup>o</sup> showed high accumulation in colon and effectively scavenged ROS in colitis mice.<sup>1)</sup> We hypothesize that combination of anticancer drugs with RNP<sup>o</sup> is a promising strategy to improve anticancer effect and minimize unwanted adverse effects.

We investigated that accumulation of orally administered RNP<sup>o</sup> is significantly higher in cancer tissues than in healthy colon tissues, resulting in a high therapeutic effect and extremely low intestinal toxicity with this nanotherapeutics. Even when a high dose of RNP<sup>o</sup> was given orally for 1 month, no toxicities were observed in the intestinal tract or other organs. After 70 d treatment, CAC model mice induced by AOM/DSS exhibited a remarkable increase in tumor

score. Interestingly, when Iri administered was in combination with free drinking RNP<sup>o</sup>, a remarkable suppression of tumor growth was observed in mice treated with combination compared to mice treated with Iri alone (Fig. 2 left). The ROS levels were significantly suppressed in mice treated with combination of Iri+RNP<sup>o</sup>



Fig.1. Schematic illustration of Redox nanoparticle, RNP<sup>o</sup>.



Fig. 2. Effect of RNP<sup>o</sup> to colitis-associated colon cancer in mice.

compared to mice treated with Iri alone, suggesting that RNP<sup>o</sup> enhances anticancer activity of Iri by scavenging overproduced ROS in tumor environment, suppressing cancer resistance to Iri. In addition, the mice receiving Iri alone exhibited severe diarrhea scores, weight loss, and neutropenia. These adverse effects were remarkably reduced in RNP<sup>o</sup>-treated mice (Fig. 2 right). These results indicate that oral administration of RNP<sup>o</sup> not only significantly enhances the anticancer efficacy of Iri against CAC development, but also effectively suppresses the severe adverse effects of Iri.

(2) Preparation of redox injectable gels (RIG) and application for high-performance anti-adhesives.

Tissue adhesions are serious issues after surgical procedures because it initiates inflammation and oxidative stress to the peritoneal surface of organs. which induces severe clinical disorders. For this issue, we newly designed redox injectable gels (RIG), which possess nitroxide radicals as a reactive oxygen species (ROS) scavenger for high performance anti-adhesion agent. The redox flower micelles exhibiting gelation under physiological conditions were prepared by a polyion complex between polyamine-PEGpolyamine triblock copolymer possessing nitroxide radicals as a side chain of polyamine segments and poly(acrylic acid). The prolonged retention in abdominal cavity increased the effect of RIG as a physical barrier, preventing the adhesion between tissues. In addition, because RIG possesses nitroxide radicals, the gel was confirmed to scavenge excessively generated ROS and effectively suppressed inflammation generated in talc-induced adhesion model mouse. Due to the combination of physically separation and biologically elimination of generated ROS. RIG dramatically inhibited adhesion formation as compared with commercial anti-adhesion agent (Seprafilm®; Genzyme, Cambridge, MA; Fig. 2). Gelation system under physiological condition might also be suitable for antiadhesion agent on the occasion of delicate surgical operation using endoscope, catheter and even robot.

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

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#### 1. Outline of Research

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

#### 2. Research Activities

# (1) Formation of cell aggregates and their use to model tumor metastasis.

Current thrusts in nanomedicine research are directed towards the design of nanostructured surfaces able to reproduced *in-vitro* the three-dimensional environment experienced by cells. In this context, we are using three-dimensional cell aggregates as model of tumor invasion and metastasis. Chitosan-phosphorylcholine (CHPC) coatings were employed to induce cellular aggregation. Through physicochemical measurements and *in-vitro* studies, we demonstrated that the level of cellular aggregation can be adjusted by changing the amount of PC groups linked to chitosan (Fig. 1 top).<sup>1)</sup>



Fig. 1. (Top) Structure of chitosan-phosphrylcholine (CHPC), representation of a CHPC film able to promote cell aggregation and effect of PC content on the adsorption of fibrinogen on CHPC films. (Bottom) (A) Tube membrane formed between a cell and a cell aggregate. Spreading of a cell aggregate incubated with nanoparticles (B) bright field and (C) confocal microscopy (fluorescence of nanoparticles and actin fibers are red and green, respectively).

We have initiated an experimental and theoretical study (with Prof. F. Brochard-Wyart, Curie Institute, Paris, France) of the spreading of cell aggregates as a model of metastasis. We observed that, upon deposition on glass substrates, cancer cell aggregates emit membrane tubes that eventually retract or rupture (Fig. 1, bottom A). The dynamics of tube formation and retraction, interpreted in the framework of membrane mechanics, provide strong evidence that even very cohesive cells can escape aggregates, which *in-vivo* corresponds to the epithelial mesenchymal transition and tumor metastasis. We are currently assessing the dynamics of cell aggregates in the presence of nanoparticles, in an effort to model the effect of therapeutic nanoparticles on the fate of tumors (Fig. 1 B, C).

# (2) Engineered boron nitride nanotubes (BNNT) for theragnostics applications.

We have undertaken (with Prof. D. Maysinger, McGill Univ. Montreal) a study of the use of BNNTs as slow release delivery agents of curcumin, an anti-inflammatory drug. Since long NTs can cause cellular damage, it is critical to control the length of BNNTs. We devised a facile and scalable fractionation by length of BNNTs (with Dr. D. Golberg, MANA, NIMS) based on the emulsification and creaming of an oil/water/surfactant /BNNT mixture.<sup>2)</sup> The length separation is based on the fact that BNNT-coated oil droplets move towards the upper surface of the emulsion or towards the bottom depending on their density. Since the length of the BNNTs adsorbed on the droplets correlate with the droplets size, selective length fractionation of the BNNTs can be achieved (Fig. 2). This method may potentially be extended to other high aspect ratio nanomaterials exhibiting emulsification properties similar to those of BNNTs.



Fig. 2. Representation of the BNNT length fraction (a) initial oil/water mixture, (b) homogenized emulsion and (c) creaming emulsion and optical micrographs of fractionated BNNTs.

#### (3) Water-dispersible long-lived NIR emitting silicon QDs.

Semiconductor QDs used for *in-vitro* and *in-vivo* imaging may never be used clinically due to concerns about their toxicity and long term stability.<sup>3,4)</sup> We have developed a scalable, one-step route to prepare water dispersible NIR emitting Si QDs from organophilic SiNPs (with Dr. N. Shirahata, MANA, NIMS). These SiNPs exhibit spectral tunability, high quantum efficiency, photostability, and low toxicity. They may serve as efficient NIR probes for deep tissue imaging *in-vivo*, in view of their exceptional long luminescence decay profile and two-photon excitation capability.

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## Next-Generation Semiconductor Nanodevices

Group Leader (Nano-Materials Field) Naoki FUKATA



#### 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. Functionalization of semiconducting SiNWs by impurity doping is one of the important processes for their application as next-generation field effect transistors. In order to control the dopant concentration, distribution, and electrical activation, it is necessary to characterize the bonding states, electronic states, and electrical activities of dopant atoms.<sup>1-4)</sup> In addition to these, it is also important to understand the behaviors of dopant atoms during thermal oxidation in the fabrication of gate dielectric films of ultra large scale integrated circuit (ULSI). Thermal oxidation using ozone gas is one of the possible solutions to achieve a good quality of SiO<sub>2</sub> layer at low temperature.<sup>59</sup>

#### 2. Research Activities

#### (1) Structural change by thermal oxidation.

SiNWs were grown by catalytic laser ablation. Representative TEM images of SiNWs before and after ozone oxidation at 600°C are displayed in Fig. 1a and 1b and nicely show how the oxidation time was used to control the effective diameter of the wires, as also pictorially illustrated in Fig. 1d. This is clearly seen in Fig. 1b where the ozone oxidation effectively increases the thickness of surface oxide layer, resulting in the decrease in the Si crystalline core region. It is noteworthy that thermal oxidation occurred at the low temperature of 600°C. We also performed thermal oxidation at 500-900°C in  $O_2$  gas atmosphere, which,



Fig. 1. High-resolutional images of SiNWs (a) before oxidation and after (b) ozone oxidation at 600°C and (c) normal oxidation at 900°C. The oxidation times are 180 min. (d) A schematic illustration of thermal oxidation of SiNWs. (e) Dependence of the thickness of the surface oxide layer on oxidation temperature.

hereafter, we refer to as normal oxidation. No significant changes were observed after normal oxidation below 600°C, while the SiNWs were thermally oxidized at higher temperature than 600°C as shown in Fig. 1c. The enhanced oxidation rate by ozone oxidation at low temperature is due to the release of the first-excited state of oxygen atoms O (<sup>3</sup>P) from O<sub>3</sub> by a thermal decomposition reaction at a Si surface. The dependences of the thickness of surface oxide layer on oxidation temperature are summarized in Fig. 1e.



Fig. 2. (a) Dependence of the peak intensity of <sup>11</sup>B local vibrational peak (shown in (b)) on ozone oxidation time. (c) Dependence of the ESR signal intensity of conduction electrons on ozone oxidation time. (d) ESR signal observed for codoped SiNWs before oxidation. The deconvolution result of the ESR signal is shown as dotted lines (red: conduction electrons, blue: P<sub>b</sub> type-defect).

#### (2) Segregation behaviors of B and P in SiNWs.

The segregation behaviors of B atoms can be investigated by using the local vibrational mode of <sup>11</sup>B atoms (Fig. 2b). For singly B-doped SiNWs, B atoms easily segregate to the SiO<sub>2</sub> side, while they can stay at the Si side by pairing with P atoms in codoped SiNWs during thermal oxidation carried out at less than 800°C (Fig. 2a). The B-P pairing was dissociated by oxidation at above 800°C (Fig. 2a, c). These observations were corroborated by first-principles calculations which demonstrated that the B-P interaction stabilizes the B atom in the Si side, inhibiting its diffusion to the oxide (Fig. 2e). This phenomenon is not a simple compensation, but rather dopant passivation due to the formation of a B-P chemical bond. In SiNWs with smaller diameters, the B-P pairing seems to occur with a higher probability and show different dopant dynamics during thermal oxidation compared to bulk Si.

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## **Development** of Nanomedicines

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

#### Nobutaka HANAGATA



#### 1. Outline of Research

Cytosine-phosphate-guanosine (CpG) DNA can induce innate and adaptive immunity through their recognition by Toll-like receptor 9 (TLR9) that is localized in the endolysosomes of antigen presenting cells. Therefore, CpG DNA can be used in immunotherapy for various diseases including infectious diseases, allergies, and cancer. Recently, it is reported that DNA recognition receptors, cGAS, IFI16, and DDX41, also exist in cytosol. These cytosolic DNA receptors recognize double-strand DNA in a DNA sequence independent manner. The sequence independent recognition in these cytosolic DNA receptors cause autoimmune disorders when the receptors sense self-DNA released from apoptotic or necrotic cells. One of targets in my study is the development of CpG DNA delivery system using nanocarrier to protect the DNA drug from degradation by DNase. Another target is development of DNA drug to inhibit self-DNA recognition by cytosolic DNA receptors.

#### 2. Research Activities

(1) Development of intracellular delivery system for DNA drugs.

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 drug must be retained in the endolysosome for a long period of time because the TLR9 is localized in the endolysosome. Therefore, delivery system using CpG



Fig. 1. Nanocarriers for CpG DNA delivery. Mesoporous silica (left) and silica-chitosan hybrid (right).

DNA drug require a design strategy different from conventional drug delivery system. We have developed nanocarriers such as mesoporous silica<sup>1,2)</sup> and silica-chitosan hybrid,3) for CpG DNA drug delivery (Fig. 1). The CpG DNA delivered by these nanocarriers demonstrated better performance for immunostimulation than conventional cationic liposomes.

#### (2) 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 receptor proteins such as cGAS, Ifi16, and DDX41, 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- $\beta$  (IFN- $\beta$ ). 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 mediator cytokines using synthetic oligodeoxynucleotide (ODN) that has a higher affinity to the DNA receptors than self-DNA. Although single-stranded natural phosphodiester ODN had no potential to inhibit the binding of self-DNA to the receptors, single-stranded artificial phosphorothioate ODN showed the inhibition effect in both immune and non-immune cells. On the other hand, natural phosphodiester ODN containing CpG sequence had a potential to inhibit the binding of self-DNA to the receptors in non-immune cells. This result can be applied to the DNA drug delivery using nanocarriers for the treatment of autoimmune disorders.

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## **Bioactive** Ceramics Materials

Group Leader (Nano-Life Field)

#### **Masanori KIKUCHI**



#### 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 (Fig. 1). 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.<sup>1)</sup> This material is now commercially available in Japan as "Refit<sup>®</sup>," and is very welcomed from orthopedic surgeons. 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.



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

#### 2. Research Activities

#### (1) Injectable HAp/Col materials.

Injectable artificial bone with bioresorbability is strongly desired in practical medicine to realize good minimum invasive surgery to reduce potential risk of bone fractures as well as inhibition of new bone formation due to remaining of cements in body. Injectable HAp/Col could be good candidate because of its nature to reduce these risks. We utilize sodium alginate (Na-Alg) for gelation and lubrication agent for injectable HAp/Col.<sup>2)</sup> This year, we focused on

calcium compound with appropriate solubility. Addition of more than 8x equivalent amounts calcium citrate (Ca-Cit) to Na-Alg showed anti decay property as well as tolerant viscosity for operation by cooperative reaction of released Ca<sup>2+</sup> ion and citrate; however more than 12x addition, effect of citrate became dominant to form acidic gel. In addition, all anti-decay paste showed decreasing in pH after antidecay test. To solve that, CaCO<sub>3</sub> was also added with Ca-Cit, and we successfully obtained pH maintained anti-decay self-setting HAp/Col paste. In addition, all ant-decay selfsetting HAp/Col paste, including no CaCO<sub>3</sub> addition ones, showed no significant cell proliferation suppression except for 12x Ca-Cit addition as shown in Fig 2.



Fig. 2. Cell proliferation curves for MG63 cells cultures with selfsetting anti-decay hydroxyapatite/collagen paste, which were previously set in incubator. Note: 8x to 12x meant calcium citrate amounts and 8x-2x to 12x-2x meant calcium citratecalcium carbonate amounts.

#### (2) Scaffold for osteochondral tissue.

Mosaicplasty is most successful surgical technique to repair large chondral defect by transplantation of articular cartilage with subchondral bone, osteochondral tissue, from non-sliding site; however, this method has demerits at donor site as the same as the other transplantation techniques. Although many researchers tried to prepare osteochondral scaffold using hydroxyapatite (HAp) or other ceramics, they have still problems on both chondral and subchondral parts. We tried to use the HAp/Col sponge as subchondral part to enhance bone regeneration properties and bioresorbability. We successfully fabricated viscoelastic bi-layered scaffold of collagen and the HAp/Col with sufficient mechanical proeperties and cytocompatibility.

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## Materials for Functional Nanomedicine

Group Leader (Nano-Life Field)

#### Hisatoshi KOBAYASHI



#### 1. Outline of Research

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

#### 2. Research Activities

(1) Usefulness of a Fibroin Nanofiber Non-woven Mat as an Artificial Cornea.<sup>1)</sup>

Artificial corneas have been studied in various ways, but promising materials or methods have not yet been established specifically for the corneal stroma. Anatomically, the corneal stroma consists of precisely aligned collagen layers and keratocytes. This unique structure is thought to be associated with corneal transparency. Here, we investigated the use of fibrous material as an artificial corneal stroma.

Aligned nanofiber non-woven mats can easily be fabricated from an aqueous fibroin solution by using an electrospinning technique. Aqueous silk fibroin solution (9-12 wt%) was donated from National Institute of Agrobiological Sciences. For preparation of electrospinning solution, 8 wt% fibroin aqueous solution was gently mixed with a 5 wt% poly (ethylene oxide) aqueous solution in the volume ratio 4 to 1. An electrospinning system equipped with a rotation drum collector (NANON, MECC Co., Ltd., Japan) was used to fabricate aligned non-woven mats as following setting; applied voltage was 12 kV, a feeding rate was 0.3 ml/h, a spinning distance was 185 mm, a stainless needle was 25 G, a diameter of the drum collector was 100 mm, rotation speed was 3000 rpm and spinning time was 3 hours. An aluminum foil was wound around the rotation drum as a collector. Humidity in the NANON was kept below 25 % by nitrogen gas perfusion. For insolubilization, electrospun aligned fibroin fiber mat was immersed into dehydrated ethanol for 24 hours. After insolubulization



Fig. 1. Immunohistostaining of Keratocyte adhered to fibroin nanofiber non woven mat in vitro, 2 weeks after culture. a) HE stainning, b) DAPI staining, c) alpha-SMA staining.



Fig. 2. Optical images of the animal operation, 3 weeks after implantation in vivo. a) Gross appearance of Fibroin fibroin fiber implantation. b) HE stainning, c) Fibroin fiber anti-Vimentin stainning, d) Fibroin fiber anti alpha smooth muscle actin staining.

process, containing poly (ethylene oxide) was eliminated by immersing into 95% ethanol and distilled water for 24 hours. Then, insolubilized fiber mat was sterilized by autoclave (ES-215, TOMY SEIKO Co., LTD., Japan) treatment at 121 degree Celsius for 20 minutes. We evaluated the possibility of using our aligned electrospun fibroin nanofiber mat as a novel artificial corneal stroma. From in vitro experiments (Fig. 1), seeded corneal stromal cells migrated into the space of the fibroin fiber mat as well as adhered to the surface. These migrating and adhering cells kept its phenotype. Similar phenomena also confirmed in vivo implantation test (Fig. 2). Three weeks after surgery, host-derived corneal stromal cells were migrated into implanted fibroin fiber mat. Inflammatory or immune responses against the implanted fibroin fiber mat were not seen till 3 weeks after surgery.

These findings strongly suggest that our fibroin aligned fiber mat will be useful as an artificial cornea.

#### Acknowledgement

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## Functionalization of Atomic Network Materials

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



#### 1. Outline of Research

Approximately two thirds of primary energy (fossil fuels, etc) being consumed in the world, sadly turns out to be unutilized, with much of the waste being heat. The direct conversion of waste heat to electricity is a large incentive to find viable thermoelectric (TE) materials.<sup>1)</sup> Traditionally, high performance TE materials have tended to not be element friendly; being composed of Bi, Te, Pb, etc. 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.<sup>2-4)</sup>

#### 2. Research Activities

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

Boron forms analogous structures (clusters and sheets) to the more famous carbon materials ( $C_{60}$  fullerenes and GIC & graphene), but a large difference is the electron deficiency which causes these boron structures mostly to form in combination with metal atoms.<sup>2-4)</sup> In any case, higher boride cluster compounds are predominantly p-type. A series of homologous RE-B-C(N) compounds was previously discovered to be the long awaited n-type counterpart to boron carbide. This year, the origin of the anomalous n-type behavior in Y-B-C(N) was discovered to be related to the pseudo-gap electronic structure formed mainly by the boron cluster framework (Fig. 1).<sup>5)</sup>

Finding good p, n matching materials has been one of the large obstacles for TE application. Through particular synthesis processes, we have achieved excellent control of p-n characteristics (+400  $\mu$ VK<sup>-1</sup> to -200  $\mu$ VK<sup>-1</sup>) in YAlB<sub>14</sub> by varying the Al site occupancy. Thereby is achieved p, n control with same crystal structure (*i.e.*, good matching) and no necessity for foreign element doping (*i.e.*, no migration problems).<sup>6</sup> Further enhancements of TE properties were investigated, while the surprising discovery of variable metal



Fig. 1. Electronic structure of Y1., B295C4.

site occupancy in a boride was also theoretically elucidated.<sup>7</sup> Complete removal of Al was done to obtain YB<sub>25</sub> which showed a Seebeck coefficient of 1000 µV/K at 300 K, and the Al-rich limit was also tested.<sup>8)</sup> Densification and microstructure control of this compound was also achieved by utilizing SPS and doping.9 Such high temperature TE materials are expected to be utilized as topping cycles for power plants and focused solar TE generation.

(2) Cage compounds for TE.

Cage compounds skutterudites are one of the most studied TE materials in the world, hoped to be used in vehicles, etc. We developed novel skutterudites which exhibited high TE performance despite being rare earth-free (not dependent on the "rattling" mechanism) and with good resistance to oxidation.10)

(3) Layered materials and MBE.

In layered materials, we have shown that controllable nanoscale building defects are a mechanism to substantially reduce thermal conductivity.<sup>11)</sup> It is also striking that in AlB<sub>2</sub>, which structure-wise is graphene boron sandwiching Al atoms, we showed that the thermal conductivity is actual larger perpendicular to the graphene-like layers.<sup>11)</sup> MBE of TE materials in order to utilize and definitively prove the "confinement" effect is being carried out, and high quality nitride materials were fabricated. For material design, calculations show that AMN<sub>2</sub> layered complex metal nitrides with both 2D and 3D electronic structures may be superior to the well-known oxides like SrTiO<sub>3</sub>.<sup>12,13)</sup>

#### (4) New concepts for TE enhancement.

We investigated near the phase boundaries of a chalcogenide with complex phases of CDW and superconductivity in search of new concepts of high TE. No high TE was found, but as a striking by-product of the research, the origin of the phases was elucidated.<sup>14)</sup>

(5) Other properties (superconductivity).

In collaboration, the low-energy Einstein-like phonon mode was shown significant for superconductivity in  $YB_{6}$ .<sup>14</sup>

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## Control of the Infrared Light in Nanospace

Group Leader (Nano-System Field) Tadaaki NAGAO



#### 1. Outline of Research

The technology for amplifying, confining, and scattering the light in nanoscale is strongly desired as a key technology in communication, optical sensing, and energy harvesting. Plasmonics and metamaterial are now accepted as useful paradigms for materials science which enable us to control flexibly the light in nanospace. Through this concept we have been developing some materials with extraordinary signal enhancement of molecules, enhanced photocatalytic reaction, and smart solar power harvesting. Our laboratory investigated the functions of thin nanomaterials that are dramatically smaller than the wavelength of light, focused wherein a large number of atoms and electrons oscillate dynamically in a collective manner.

#### 2. Research Activities

Here in our laboratory we aim at manipulating the infrared light waves for enhancing the applications in environmental monitoring as well as solar and thermal energy conversion by developing the new metallic nanostructures. We also focused ourselves to the fabrication of various metal-oxide or oxide-oxide nanocomposite material 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. 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. (a) An electromagnetic simulated of the electric field at a nanogap between the Au islands. A schematic illustration of the DNA aptasensing of pathogenic proteins.

In infrared absorption spectroscopy of aqueous solutions, the large signal of the water itself is an obstacle which makes it difficult to measure trace amounts with high sensitivity. One can avoid this problem by utilizing the strongly-enhanced plasmonic nearfield generated at the nanogaps of Au nanostructures to selectively detect the molecules entered in the nanogaps while suppressing the signal of the bulk water. By forming a gold nanogap structure, in which the targeted protein molecules have a width on the order of 2 or 3 target molecules, and coating molecules called DNA aptamers, which strongly bond with the target molecules in the nanogap structure, selective detection of trace amounts of pathogenic enzymes and ionic species mixed in water was possible (Fig. 1).<sup>1)</sup>

Infrared perfect absorbers, which can absorb 100% of infrared radiation, have the potential for use in various applications such as sensing of organic molecules in liquids and gases, generation of electricity using thermal radiation as an energy source, etc. We developed a simple lithography method using inexpensive base metals and ceramics, in which microspheres are used as a mask material, and developed a technique for fabricating IR perfect absorbers with high accuracy utilizing this method (Fig. 2). Using this fabrication method, we realized sharp wavelength-selective IR absorption and high sensitivity molecular sensing, and we are also started to study thermal radiation.<sup>2,3)</sup>



Fig. 2. An SEM micrograph of a mid-infrared plasmonic perfect absorber and a photo of a large-scale sample. Its absorption efficiency is > 98% and its thermal emission was confirmed to be monochromatic in the wavelength region from 4 to 10  $\mu$ m.

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

#### 2. Research Activities

# (1) Mono Si growth using seed cast method for solar cells (Square-Si).

We have been developed seed cast growth technique (Fig. 1) to supply monocrystalline (mono) Si for photovoltaics. The mono Si ingot of 50 cm square was grown from one single crystalline Si seed of 20 cm diameter. Not only the growth furnace but also the gas flow condition has been optimized to produce high quality mono Si. The light element impurities, such as C and N, have been reduced to suppress precipitation. The thermal history, especially cooling procedure, has been optimized to suppress dislocation generation.<sup>1)</sup> Such efforts have realized the new mono Si of high efficiency and low cost.



Fig. 1. Schematics of (a) multi and (b) single seed cast method, and (c) grown Si ingot of single seed cast.

# (2) Dislocation evolution in widegap materials, SiC and GaN (Multi-dimensional EBIC & Anything CL).

SiC and GaN are expected as the materials for power devices. For the device application of these materials, the suppression of extended defects is the key to improve



Fig. 2. Schematics of killer defects in SiC and GaN.

efficiency. However, the killer defects are different in these materials. The killer defects in SiC are the screw dislocations running along c-direction and stacking faults. On the other hands, the edge dislocations are the killer defects in GaN. Such difference was discussed in terms of growth mechanism, Burgers vector, and surface roughness (Fig. 2). The understanding of the defect nature is necessary to control them to improve the quality of power devices.<sup>2)</sup> As for the observation of dislocations, EBIC is the suitable method to image the dislocations in SiC, while CL for GaN (Fig. 3).



Fig. 3. (a) EBIC image of dislocations in SiC and (b) CL image of those in GaN.

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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.<sup>1)</sup> 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

NPs 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 (Fig. 2). And this FHDS mainly includes inflammatory response, stress response, and genotoxic response. In nature, different reasons could cause genotoxic response to DNA damage, such as ionizing radiation, ultraviolet light, and oxidizing agents. B-cell translocation gene 2 (BTG2) is implicated in



Fig. 2. "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.

cell cycle regulation, DNA repair, apoptosis and senescence. TiO<sub>2</sub> NPs were used to detect their induced potential genotoxic response using BTG2 sensor cells. The BTG2 sensor cells show that NPs can induce high genotoxic response. The modifying TiO<sub>2</sub> NPs by polyethylene glycol (PEG) reduced genotoxic response (Fig. 3).<sup>2)</sup> The results were useful for safer NPs development.



Fig. 3. Comparison of BTG2 responses induced by TiO<sub>2</sub> and PEG-TiO<sub>2</sub> NPs.

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## Nano-System Computational Science

Group Leader (Nano-Power Field)

#### Yoshitaka TATEYAMA



#### 1. Outline of Research

We are challenging to make novel theoretical frameworks for physicochemical phenomena such as electron transfer, proton transfer & photoexcitation (Fig. 1), 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, and Li-ion battery.



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

#### 2. Research Activities

Recent results are illustrated in Figs. 2-5 for Lithium ion battery projects (Fig. 2), photovoltaic projects (Fig. 3), electrode interface projects (Fig. 4) and methodology projects (Fig. 5).



Initial Stage of Charging (Li ion concentration)

Fig. 2. Schematic pictures of our results on (upper) unusual stability against electrolyte reductive decomposition in highlyconcentrated Li-salts electrolyte,<sup>1,2)</sup> and (lower) space-charge layer mechanism at interface between the oxide cathode and sulfide electrolyte and the buffer layer effect<sup>3)</sup> in our Lithium ion battery projects.



Fig. 3. Interfacial states of (left) dye-sensitized solar cell<sup>4</sup> and (right) perovskite solar cell<sup>5</sup> in our photovoltaic projects.



Fig. 4. Interface and surface states at the semiconductor electrodes of (upper) boron-doped diamond<sup>6</sup> and (lower)  $SrTiO_3^{7}$  in our electrode interface projects.



Fig. 5. Schematic picture of new QM/MM method for full electron transfer reactions between donor and acceptor<sup>8</sup> in our methodology projects.

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## In-Situ Bandgap Tuning of Graphene Oxide Achieved by **Electrochemical Bias Group** Leader

(Nano-System Field) MANA Research Associate Kazuya TERABE

Takashi Tsuchiya



#### 1. Outline of Research

Not only fabrication scale for the conventional semiconductor devices, but also the physical operating is being reached limit in near future. One possible way to overcome these technological and physical limits of the existing conventional semiconductor device is to achieve breakthroughs in device materials and novel deviceoperation principle using nanotechnology. A promising type of such nano-devices is the nano-ionics device,<sup>1)</sup> which is operated by controlling the local ion migration and electrochemical reaction instead of electron and hole migration.

It is known that graphene oxide (GO) sheets are useful for ultrathin, flexible nano-electronic devices, and display unique properties including photoluminescence and room temperature ferromagnetism. The ability to modulate the physical properties of GO within electronic components could can has numerous applications in technology.

In this research, we have developed a novel nano-ionic technique that allow to fine tune the physical properties of GO, such as electrical conductivity and photoluminescence, and create the functional nano-ionic devices based on GO.

#### 2. Research Activities

The conductivity of GO is lower than graphene itself because of disruptions within its bonding structure. Specifically, the carbon atoms in GO exhibit a blurring of energy levels called sp<sup>2</sup> or sp<sup>3</sup> hybridizations (Fig. 1a). In ordinary GO, bonding in the sp<sup>2</sup> level is disrupted, and under severe disruption the GO becomes an insulator rather than a conductor. In contrast, highly-reduced GO (rGO), with lower oxygen levels, has a near-perfect hexagonal lattice structure with strong bonds and high conductivity. By adjusting the percentages of  $sp^2$  and  $sp^3$  domains in GO, we have gained the ability to fine tune band gaps and therefore control conductivity.

We have achieved the non-volatile tuning of bandgaps in



Fig. 1. (a) Graphene oxide structure, (b) Schematic illustration of GObased ionic transistor with YSZ proton conductor. Brown and green circles represent positive and negative charges accumulated at interfaces due to proton migration. H<sup>+</sup> represents positively charged proton.

multi-layered GO within an all-solid-state transistor using nano-ionic operation.<sup>2)</sup> The ionic transistor comprised GO on a silica glass substrate is gated using proton migration in yttrium stabilized zirconia (YSZ) conductor (Fig. 1b). The treatment triggers a reversible electrochemical reduction and oxidation (redox) reaction at the GO/zirconia interface by applying a dc voltage. This in turn caused proton migration at GO surface through the zirconia. The redox reaction created rGO, and caused an increase in current between the drain (D) and source (S) electrodes in the transistor.



Fig. 2. (a) Optical microscope images of gate-voltage-applied GObased ionic transistor. (b) DC bias dependence of optical band gap measured by UV-vis-near IR reflectance spectroscopy and calculated to be from 0.75 to 0.30 eV.

As shown in Fig. 2a of optical microscope images of gate-voltage-applied GO transistor, the rGO region can be easily distinguished from the GO region. GO is transparent before applying gate bias.<sup>3)</sup> The color of area around D and S electrodes changes grey after applying bias voltage. Micro-XPS and Raman spectroscopy reveals rGO forms in this area, which indicate the reduce reaction of GO.

It is interesting to note that nanoionic motion of protons at the GO/YSZ interface resulted in both sp<sup>2</sup>/sp<sup>3</sup> fraction variations in the GO. It is confirmed that resistive switching operation can be achieved by tuning the band gap using reversible redox reaction of GO. The potential application of the reversible and in situ tuning of the  $sp^2/sp^3$  fraction includes not only transistor but also optical, photoluminescent,<sup>4)</sup> magnetic, and superconducting devices. To explore new functions in carbon materials, work is underway to extend this method to the in situ tuning of the sp<sup>2</sup>/sp<sup>3</sup> fraction not only in other sp<sup>2</sup>-hybridized systems such as carbon-nanotube, fullerene, and graphite systems, but also to sp<sup>3</sup>-hybridized systems such as diamond.

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## Effect of Living Cells on the Biodegradation of Mg Alloys

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



#### 1. Outline of Research

Magnesium and its alloys are expected to be used as biodegradable implant devices since they are easily corroded by reacting with water in the body fluid. For the success of their biomedical application, it is important to control their degradation ratio in the human body environment since it influences not only their mechanical integrity along the implantation period but also their biocompatibility. To achieve the ideal degradation rate of Mg alloy devices, it is mandatory to understand their degradation mechanism in biological environment.

Body fluid contains inorganic ions as well as organic compounds such as amino acids and proteins. Implanted devices are also facing to surrounding tissues and cells. We have already reported the accelerating and inhibiting effects of amino acids and serum proteins on pure Mg biodegradation under cell culture condition.<sup>1)</sup> In this study, the effect of cells on the degradation of a Mg alloy is examined by an electrochemical measurement.<sup>2)</sup>

#### 2. Research Activities

In vitro degradation behavior of a Mg-1wt%Ca alloy was studies with and without culturing cells (murine fibroblasts L929) in Eagle's minimum essential medium supplemented with 10% fetal bovine serum (E-MEM+FBS) under cell culture condition, i.e., 37°C and 5% CO<sub>2</sub> in humidified air. A standard three-electrode system was employed, which consists of a Mg-Ca alloy sample (exposed area of 0.950 cm<sup>2</sup>) as a working electrode, Ag/AgCl (3M NaCl) as a reference electrode and a platinum mesh as a counter electrode. Electrochemical impedance spectroscopy (EIS) was performed under following conditions; at OCP, 5mV, 0.01~10<sup>5</sup> Hz after 6, 24 and 48h of incubation. Fig. 1 shows typical EIS results of Mg-Ca alloy samples with and without cells. The equivalent circuit model used to analyze EIS spectra and resulting polarization resistance  $(R_p)$  were shown in Fig. 2a.  $R_p$  was calculated by adding  $R_{pore}$  and  $R_{ct}$ .  $R_p$  without cells



Fig. 1. Nyquist plot of Mg-Ca alloy samples in E-MEM+FBS with and without living cells (abbreviated as WC or WOC, respectively) up to 48h incubation at 37 °C in 5% CO<sub>2</sub>.



Fig. 2. (a) Polarization resistance (Rp) of Mg-Ca alloy samples in E-MEM+FBS with and without living cells (abbreviated as WC or WOC, respectively) up to 48h-incubation, and (b) Mg<sup>2+</sup> release into the medium after 48h-incubation.

increased from 6 to 24h and remained stable at 48h whereas  $R_p$  with cells decreased along the incubation period

After the EIS measurement, Mg<sup>2+</sup> release into the medium was quantified by a colorimetric kit following its instruction. As shown in Fig. 2b, higher  $Mg^{2+}$  release was observed from the sample with cells than that without cells. Cells on the sample surface was fixed and stained for an optical microscopic observation, and then, removed by acid cleaning. Fig. 3 shows the sample with cells before and after cell removal. Severe localized corrosion was observed on the sample surface beneath the cell colonies. The pH of the medium after 48h-incubation with and without cells was 7.37 and 7.66, respectively. This slight lower pH for the sample with cells probably causes the reduction of R<sub>p</sub> and severe localized attack beneath the cells, resulting in the higher  $Mg^{2+}$  release than that without cells. Obtained data revealed the accelerating effect of cells on the biodegradation of a Mg alloy and suggests the importance of biological factors to estimate the degradation rate of Mg alloys for implant application.



Fig. 3. Optical microscope images of a Mg-Ca alloy sample after 48hincubation with cells (left) and after the removal of cell colonies by acid cleaning (right). The lines in the right images indicate the place of cell colonies.

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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 solid surfaces and two-dimensional systems. Currently, we concentrate on developing laserphotoemission spectroscopy (PES) into a novel technique to probe surface dynamics. Vibrational dynamics of adsorbatesubstrate 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.

We found that the photoemission spectra excited by the low energy laser light contain the vibrationally induced inelastic components. This result indicates that the laser excited and low-energy photoelectron strongly interacts with vibrational elementary excitations. We believe that this inelastic interaction bring us a novel way to investigate dynamics arising from the electron-phonon couplings. Thus one of the aims of this research project is developing the laser-PES as a reliable tool for measuring electron-phonon coupling.

Another important subject of this research project is searching for a new two-dimensional material in which novel quantum characters explicitly appears. I believe that such material is a good sample for the laser-based PES technique.

#### 2. Research Activities

(1) 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).

#### (2) Decoupling of electronic hybridization of novel twodimensional material with substrate.

Carbon and silicon are members of the 14<sup>th</sup> group in the 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 exist in nature. Silicene, two-dimensional honeycomb sheet consisting of Si atoms, is a new type allotrope of Si. As

silicene attracts much attention as a new low-dimensional material because its 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 (known as two-dimensional topological insulator, at present) and the high compatibility with the current Si device technology triggers the competition to realize the silicene. Recently, we have succeeded in fabricating silicene on Ag(111) substrate. Unfortunately, we found that the electronic character of silicene loses its exotic nature by interacting with metal substrate.

Geometrical and electronic structures of silicene on Cu(111) covered with the monolayer of hexagonal boron nitride (h-BN) were investigated by ab-initio density functional theory calculations. We found that a  $\sqrt{3} \times \sqrt{3}$ R30° silicene with a regularly buckled configuration is stabilized on  $\sqrt{7} \times \sqrt{7}$  R19.1° h-BN layer stacking commensurately to the Cu(111) substrate. The electronic band structure projected to Si 3pz orbital clearly shows a band crossing similar to a Dirac cone emerging in the band structure of freestanding buckled silicene. This is in contrast for the silicene on Cu(111), in which the Dirac fermion features, disappear entirely due to the strong interactions at the interface. These demonstrate that the h-BN layer effectively prevents silicene from interacting with the underlying Cu(111) substrate and that the h-BN monolayer on Cu(111) is a promising candidate for substrate to realize silicene hosting the Dirac fermion features (Fig. 1). Currently, we are trying to fabricate silicene on h-BN covered metal substrate, experimentally.



Fig. 1. Geometrical structure of silicene on h-BN/Cu(111). The Si atoms are represented by the blue and pale-blue balls. The pale blue ball indicates the upper Si atom. The B and N atoms are represented by green and gray balls, respectively.

## 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. 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.

We are interested in discoveries of new perovskite-type materials using advanced high-pressure synthetic technique. With that technique, new horizons can be revealed. We are aiming at finding and developing new environmentally friendly materials with ferroelectric and multiferroic properties.



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

#### 2. Research Activities

# (1) Crystal Chemistry and Physics of Perovskites with Small Cations at the A Site.<sup>1)</sup>

Synthesis, crystal chemistry, and physics of perovskites with small cations at the *A* site are an emerging field in perovskite science. ScBO<sub>3</sub> and InBO<sub>3</sub> perovskites extend the corresponding families of perovskites with A = Y, La-Lu, and Bi and exhibit larger structural distortions. As a result of large distortions, they show, in many cases, distinct structural and magnetic properties. It is manifested in *B*-siteordered monoclinic structures of ScMnO<sub>3</sub> and 'InMnO<sub>3</sub>'; an unusual superstructure of ScRhO<sub>3</sub> and InRhO<sub>3</sub>; two magnetic transitions in ScCrO<sub>3</sub> and InCrO<sub>3</sub> with very close transition temperatures; and antiferromagnetic ground states and multiferroic properties of Sc<sub>2</sub>NiMnO<sub>6</sub> and In<sub>2</sub>NiMnO<sub>6</sub>. They have many features, which were not observed in 'classical' perovksites, such as, transition metal doping into the *A* site, (Sc<sub>1-x</sub>*B<sub>x</sub>*)BO<sub>3</sub> and unconventional magnetic ground states.

#### (2) Discovery of New Perovksite Manganites.<sup>2)</sup>

Perovskite-structure rare earth manganites, of which LaMnO<sub>3</sub> is the prototype, have been a playground for solidstate and materials chemists and physicists for decades. They exhibit colossal magnetoresistance, a range of charge and orbital orderings, and diverse and coupled ferromagnetic, antiferromagnetic, insulating, and metallic properties. There is considerable motivation to extend the perovskite  $AMnO_3$ family in the search for new magneto-structural coupling behaviors. Unfortunately, however, few possibilities remain. We discovered TlMnO<sub>3</sub> and showed that its structural and magnetic properties are distinct from those of all other AMnO<sub>3</sub> manganites (Fig. 2). TlMnO<sub>3</sub> expands the AMnO<sub>3</sub> family from one hand. From another hand, it stands apart other members of the family similar to BiMnO<sub>3</sub>. Therefore, TlMnO<sub>3</sub> has potential to become a new playground in the manganite family.



Fig. 2. Crystal structure and magnetic properties of TlMnO<sub>3</sub> perovskite.

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## Interface Engineering for Improving Optical Switching in a Diarylethene-Channel Transistor MANA Independent Scientist Ryoma HAYAKAWA



#### 1. Outline of Research

The development of optical switching organic field-effect transistors (OFETs) with photochromic molecules, including diarylethene (DAE), azobenzene and spiropyran (SP), has attracted considerable attention with a view to providing a new direction for organic electronics.<sup>1,2)</sup> In most cases, self-assembled monolayers of these photochromic molecules and their mixtures with polymeric semiconductors are employed as "photoresponsive additive parts". In these devices, the drain currents through organic semiconductors have been reversibly controlled by light irradiation depending on photochromic reactions. However, the light-induced current modulations were relatively small (less than 500 %).

To overcome this obstacle, we have proposed utilizing DAE thin films themselves as the channel layers in OFETs (Fig. 1(a)).<sup>3)</sup> We proved that the DAE films with closed-ring isomers work as p-type transistor channels. The transistor channel was then completely off when the DAE molecules changed into open-ring isomers. On the other hand, our proposed OFETs have some problems involving the high threshold voltage of -64 V and the poor endurance property in repeated optical switching.

In this report, we describe the improved optical switching performance in DAE transistors by employing interface engineering, including considerable reduction in threshold voltage by the introduction of an  $\alpha$ -sexithiophene (6T) thin film underneath S-D electrodes and marked improvement in optical switching behaviors by the surface treatment of a SiO<sub>2</sub> gate insulator with poly(methyl methacrylate) (PMMA).





#### 2. Research Activities

(1) Effect of 6T layer for enhancing hole injection.

We investigated the effect of the 6T layer on improving the transistor properties. Fig. 1(b) shows the thickness dependence of the 6T layer on the threshold voltage. The introduction of the 6T layer led to a considerable reduction in the threshold voltage. Fist, the threshold voltage was markedly reduced from -64 to -6 V even for a 1.5-nm-thick 6T layer. The value was minimized at a film thickness of 3 nm and then increased moderately to -10 V at 6 nm. The result reveals that the insertion of a 6T layer between the S-D electrodes and DAE transistor channels was effective in reducing the carrier injection barrier.

To provide evidence of hole injection enhancement, we evaluated the energy-level diagram of an Au/6T/DAE multilayer using a photoelectron spectroscopy measurement. The work function of Au and he HOMO levels of the 6T and DAE layers were estimated to be -4.7, -5.2 and -5.8 eV, respectively. The determined energy diagram is shown in the inset of Fig. 1(b). These measurements showed that the HOMO level of 6T was located between that of closed-ring DAE and the work function of Au, leading to effective carrier injection from an Au electrode to DAE films.



Fig. 2. Change in the drain current in the DAE transistors ( $V_d$ = -60 V and  $V_g$ = -60V) with and without a PMMA layer against the photo-irradiation sequence.

#### (2) Effect of PMMA layer for improving optical switching.

Fig. 2 shows the optical switching of the drain current upon UV-Vis light irradiation obtained from DAE transistors with and without a PMMA layer. The drain current was measured at fixed drain and gate voltages of -60 V. A clear difference in the endurance of the photo switching was confirmed. The drain current in the sample without a PMMA layer degraded with repeated optical switching; the value had fallen by one order of magnitude after 10 cycles of photo switching. In contrast, the degradation in the drain current was effectively suppressed in the sample with the PMMA layer. These results indicate that the surface treatment of the SiO<sub>2</sub> layer with PMMA effectively suppressed the generation of defects around the SiO<sub>2</sub>/DAE interface. Our findings will provide useful ways of realizing high-performance optical switching transistors.

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## Non-Precious Metal Bi-Functional Colloidal Catalysts for Oxygen Evolution and Reduction Reactions MANA Independent Scientist Joel HENZIE



#### 1. Outline of Research

Controlling the nanoscale shape and size of colloids is of practical importance in fields including catalysis, energy storage and optics. Yet the chemical methods used to make these nanoparticles is still not well understood, even for simple unary materials such as noble metals. Shaped nanocrystals can be synthesized with precisely defined crystallographic facets that strongly influence their physical and chemical properties. My research group is developing experimental and theoretical tools to understand the mechanism of shaped nanocrystal growth in metal and metal oxide materials. The practical goal is to develop a rational and deterministic strategy for generating these shaped colloids, instead of empirical synthetic approaches based on trial and error that currently exist today. We are using these particles as building blocks for the assembly of advanced functional composite materials for energy generation and energy storage.<sup>1,2)</sup>

#### 2. Research Activities

#### (1) Modeling the Optical Properties Silver Polyhedra.

Measuring reaction kinetics in a rapidly evolving chemical reaction requires some kind of indicator to monitor the system over time. In our colloidal reaction, we are using the local surface plasmon (LSP) of the silver (Ag) nanocrystal as an indicator to track the evolution of nanoscale shapes in the reaction. This is because each shape has signature LSP absorbance peaks whose position depends on the size of the nanoparticle. We are calculating the absorbance cross-section for hundreds of shaped nanocrystals with different edge





lengths and radii of curvature using electromagnetic (EM) simulation (Fig. 1). These spectra are being used to create a machine-learning algorithm tool that can to judge the evolution of nanoparticle shape and size in a reaction in real-time. This will enable us to understand the mechanism of shape-controlled nanoparticle synthesis.



Fig. 2. (a) In one of our synthetic methods, LiMn<sub>2</sub>O<sub>4</sub> powder is dissolved in a low-temperature, surfactant-assisted hydrothermal reaction and then recrystallizes into α-Mn<sub>2</sub>O<sub>3</sub> prisms. (b) SEM image of LiM<sub>2</sub>O<sub>4</sub> powder precursor and the α-Mn<sub>2</sub>O<sub>3</sub> product (c). Tilting the sample shows that the nanoparticles are elongated along one axis (d) indicating a tetragonal prism. This work was performed in collaboration with Dr. Maryam Jahan.

#### (2) Synthesis of Bi-Functional Colloidal Catalysts for Oxygen Oxidation and Reduction Reactions.

Discovery of inexpensive non-precious metal catalysts is important for the scalability of renewable energy technologies that rely on oxygen photocatalysis and electrocatalysis. One of the aims of our research is develop low-temperature routes that generate colloids with precisely defined crystallographic facets that have high activity and selectivity for specific chemical reactions. Recently we have been working on a new kind of bi-functional catalyst that can perform both oxygen evolution reaction (OER) and oxygen reduction reactions (ORR). Inspired from biological catalyst contained Mn cluster in photosystem II, we developed a lowtemperature synthetic route to generate highly facetted α-Mn<sub>2</sub>O<sub>3</sub> nanocrystals from commercial LiMn<sub>2</sub>O<sub>4</sub> powders (Fig. 2). Anionic surfactant helps dissolve the LiMn<sub>2</sub>O<sub>4</sub> powder, and controls the final shape of the nanocrystalline product. Oxygen electrochemistry measurements show these  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub> tetragonal prisms have excellent activity for OER and ORR. This simple process will enable inexpensive technologies for energy conversion.

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## All-Solution-Processed Fabrication of High Performance Thin-Film Electronic Devices MANA Independent Scientist Takeo MINARI



#### 1. Outline of Research

Current production processes for semiconductor electronic devices require huge conveyer lines and largescale 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. To achieve a sustainable society without further aggravation of such problems, the development of fabrication methods with minimal consumption of energy and materials is required. Printed electronics is considered to be highly promising because of the relatively simple solution processes involved and the reduced requirements in terms of facilities.<sup>1)</sup> However, high processing temperature of ~150 °C is required in common printed electronics, which limits use of a common flexible substrate because of the deformation caused by heat.

In this sense, we developed 'Room-Temperature Printed Electronics (RTPE)' as the new fabrication method for thinfilm electronic devices.<sup>2)</sup> The method is an ultimately low temperature process because application of heat is not required through the whole fabrication process. The room-temperature process never causes any thermal damage to the substrate. Thus it allows direct fabrication of electronic devices onto any kind of flexible materials.

#### 2. Research Activities

#### (1) Fabrication of OTFT by room-temperature printing.

Fig. 1a represents the RT printing process of OTFT arrays. Plastic film with a passivation layer was used as the flexible substrate. First, the source/drain electrode patterning was performed using a printing technique. Then the organic semiconductor layer was formed onto the channel region of the devices, here we also used a solution process at RT.



Fig. 1. a) Optical microscope images showing the fabrication procedure of OTFT array. b) Flexing the printed OTFT arrays on the plastic substrate (left). Substrate size was 40 × 40 mm<sup>2</sup>. An optical microscope image of the OTFT array (right). c) Typical IV characteristics of the RT-printed OTFT.

After the formation of the gate dielectric layer by spin coating of the polymer at RT, the top-gate electrode layer was patterned using the printing method at RT. Thus, we successfully formed fully-printed OTFT array on a flexible substrate using the RT process only (Fig. 1b).

The electrical characteristics for RT-printed OTFTs are shown in Fig. 1c. Here hysteresis-free behavior of the IV characteristics and high on/off ratio of  $10^6$  were observed. The average mobility was determined to be 7.9 cm<sup>2</sup> V<sup>1</sup> s<sup>-1</sup>, which is much higher than that of a-Si TFTs and even comparable to that of IGZO TFTs.



Fig. 2. An OTFT active-matrix array assembled on a paper substrate using the RT printing process. a) OTFT array on the paper substrate. The size of the paper was  $40 \times 50 \text{ mm}^2$ . b) Optical microscope image of the OTFT array fabricated using the RT printing technique. The inset is an enlarged optical micrograph of the fully-printed OTFT devices on paper. c) Typical transfer characteristics of the printed OTFTs on paper.

#### (2) Direct printing of OTFTs on paper.

Our fabrication method of organic electronics at RT enables formation of devices on the surfaces of heatsensitive materials because of the low fabrication temperature. To confirm the superiority of the extremely low-temperature fabrication process, OTFTs were fabricated using paper as the substrate. A commercially available photo paper (inkjet printer paper) was selected as the heat-sensitive substrate. This paper degrades at temperatures of approximately 60 °C. Thus, only a RT process could be used to fabricate fully-printed devices on the paper.

The result of fully-printed OTFTs on paper is shown in Fig. 2. First, the logo of our institute was printed on the paper surface using a home inkjet printer to confirm the identity of the substrate as paper. Then, OTFTs were formed using the room-temperature printing method (Figs. 2a and 2b). Typical IV characteristics of the fully-printed OTFTs on paper are shown in Fig. 2c. Stable operation of the OTFTs was realized without hysteresis behavior. The average mobility of the fully-printed OTFTs on the paper was estimated to be 2.5 cm<sup>2</sup> V<sup>1</sup> s<sup>-1</sup>.

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## Quantum Devices in Nanomaterials

MANA Independent Scientist Satoshi MORIYAMA



#### 1. Outline of Research

A quantum dot is a small metallic island with a single electron charging effect and zero-dimensional confined states, which resembles to the natural atom. For this reason, the quantum dot is often called an artificial atom. Although the atom-like physics is studied their interaction with light, artificial atoms can measure electron transport properties in solid state systems. Therefore, quantum dots are expected for future electric devices that can control the single-electron charge and spin states. Unique features of the quantum dot are the single electron charging effect and the quantized energy levels, and the characteristic energy for the former is the charging energy for an single electron  $(E_c = e^2/C_{\Sigma}: C_{\Sigma})$  is the self-capacitance of the dot) and is the mean zero-dimensional level spacing ( $\Delta E$ ) for the latter. The single electron devices only need the small dot size for the higher temperature application. The quantum computing devices which may use both the single electron effect and the quantized level need quantum coherence as well. 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. Our recent research activities are the realization of quantum devices in graphene-based materials. It will be expected that the fabricated nano-systems become integrated quantum circuits because of its 2-dimensional sheet structure.

#### 2. Research Activities

(1) Field-induced Quantum Confinement/deconfinement in graphene nanodevices.<sup>1-3)</sup>

Graphene quantum-dot (QD) devices are of significant research interest. In most previous attempts to fabricate such devices, the structures were etched from a graphene sheet by lithography, and the resulting devices consisted of QDs and small constrictions connected to the lead parts. We have also demonstrated double quantum-dot devices in triple-layer graphene, which exhibits single-electron transport of two lateral QDs coupled in series.<sup>4)</sup> This top– down process enables precise control of graphene device structures on a submicron scale, but the sample edge shape varies on a nanometer scale. Therefore, transport properties of graphene QD or nanoribbon devices are often dominated by edge roughness and disorder.

Here, we propose a new device structure in which graphene mesoscopic islands are perfectly isolated and metallic contacts are directly deposited onto these islands without constrictions. Such a configuration is free from disturbances due to the structural fluctuation of constrictions and allows direct contact to the mesoscopic two-dimensional electron gases system. We demonstrated that the Coulombblockade effect evolves under a uniform magnetic field perpendicular to the graphene sheet, which indicates the quantum confinement–deconfinement transition switched by a magnetic field<sup>2</sup>. A field-induced confinement or deconfinement transition should occur owing to the interplay between the gate-induced potential and cyclotron motion. We also observed an example where extrinsic effects govern the phenomena.<sup>1)</sup> We consider that the results are due to randomly charged impurity centers in graphene, in conjugation with a gap stemming from the constriction geometry that should lead to the formation of multiple QDs owing to puddles of carriers. We have discussed the theoretical scenario of our device structure<sup>3</sup>. From a theoretical point of view, the confinement and manipulation of single Dirac fermion in the device structure is related to the topology change.





Fig. 1 shows how the current evolves in a magnetic field as a function of  $V_g$  and B, at T = 0.23 K. Near the Dirac point, conductance is strongly suppressed by the magnetic field. Furthermore, several resonance peaks emerge in the hole- and electron-carrier regions. In particular, clear resonance peaks are observed in the hole-carrier region ( $V_g$  $< V_{Dirac}$ ). These peaks correspond to the Coulomb-blockade oscillations. Such a quantum confinement-deconfinement transition is corresponding to the transition between opento-closed trajectories of Dirac particles in this type of device structure. Our experimental results indicate that a Diractype particle is confined and quantum confinementdeconfinement transition is induced by a magnetic field, which is consistent with our theoretical scenario.

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## **Development** of Photoresponsive Biointerfaces

MANA Independent Scientist Jun NAKANISHI



#### 1. Outline of Research

Biointerfaceis an interface between biomolecules and materials. It plays a pivotal role in biomedical devices such as materials for drug delivery, tissue engineering, and bioanalysis. The major purpose of the present study is to develop chemically functionalized biointerfaces with photochemically active compounds and apply them for analyzing and engineering cellular functions (Fig. 1).<sup>1,2</sup>



Fig. 1. Photoresponsive biointerfaces developing in this study.

#### 2. Research Activities

(1) A photoactivatable 96-well plate: a versatile and multiplex cell migration assay platform.<sup>3)</sup>

Cell migration is a dynamic process that underlies a variety of key physiological events, such as morphogenesis, immune response, and wound healing, and has also been demonstrated to play a central role in cancer invasion and metastasis. To date, numerous in vitro migration assays have been developed to dissect the molecular mechanisms of cell migration as well as to serve as tools for discovering new drugs that regulate cell migration and block tumor expansion. Recently, however, the desire for highthroughput screening (HTS) systems for identifying new drug candidates have stimulated a demand for new platforms of multiplex assay formats. These screening techniques greatly contribute to the development of new pharmaceuticals by allowing for the evaluation of drug potencies and efficacies in terms of their ability to change cell migration rates. Additionally, multiplex assay platforms have proven to be useful for functional genomics, (*i.e.*, siRNA screening) to identify proteins involved in cell migration. The ability to evaluate migration phenotypes, such as cell morphology as well as directional persistence and collectivity, represents another important objective when elucidating cell migration machinery. Recent studies have demonstrated that cellular microenvironments, or geometrical constraints, are critical in determining the mode of collective migration or leader cell formation. In consideration of the broad range of in vivo external constraints and the dynamic features of cellular microenvironments, it is important to engineer novel multiplex cell migration assay platforms where cellular

geometrical constraints can be taken into consideration.

We developed a method for preparing a versatile and multiplex cell migration assay platform on commercial glassbottom 96-well plates (Fig 2). Cationic polylysine was adsorbed to the anionic glass surface and functionalized with poly(ethylene glycol) (PEG) bearing a photocleavable reactive group. The initial PEGylated surface is non-celladhesive. However, upon near-ultraviolet (UV) irradiation, the photorelease of PEG switches the surface from nonbiofouling to cell-adhesive. With this platform, we assayed cell migration in the following procedure: (1) create cellattaching regions of precise geometries by controlled photoirradiation, (2) seed cells to allow them to attach selectively to the irradiated regions, (3) UV expose the remaining PEGylated regions to extend the cell-adhesive area, (4) analyse cell migration with microscopy. Surface modification of the glass surface was characterized by ζ-potential and contact angle measurements. The method was applied for evaluating the effect of model drugs on migration of epithelial MDCK cells. Dose-response relationship for the cytochalasin D treatment on cell migration behavior was successfully evaluated with high reproducibility. Interestingly, the impact of blebbistatin on cell migration was dependent upon the widths of the migrating regions, resulting in both cases of migration acceleration and deceleration. These results clearly demonstrate that the cellular response to certain drugs is highly affected by their migrating geometries. Therefore, our assay method provides a useful highthroughput platform for the identification of drug candidates that have an effect on cell migration behavior.



Fig. 2. Schematic illustrations of photoactivatable 96-well plate.

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## Development of Optically and Optoelectronically Active Molecular Liquid Materials MANA Independent Scientist Takashi NAKANISHI



#### 1. Outline of Research

Softening organic/polymeric materials which have optical and optoelectronic functions is one of the most important and prospective developments in flexible organic electronics. Especially in hardly bended, foldable geometry of such optoelectronic devices and those molecular component is mandatory to be achieved in a predictable way. We also need to consider the environmental stability, such as on long-time light exposure, oxidation in air atmosphere, of the materials composed for active components in devices. Therefore, photo- and thermally stable optically/ optoelectronically active  $\pi$ -conjugated molecules, which can be also fabricated onto substrate surfaces in any shape and geometries, are highly desired to be designed and synthesized. Here I introduce my recent research activities on functional organic liquid materials.<sup>1-3)</sup>

#### 2. Research Activities

(1) Nonvolatile Liquid Anthracenes for Facile Full Color Luminescence Tuning at Single Blue-Light Excitation.<sup>4</sup>

Nonvolatile molecular liquids at room temperature that can luminesce are a new generation of organic soft materials. They possess high stability, versatile optical properties, solvent-free fluid behaviour and can effectively accommodate dopant dye molecules. With a view to flexible electronic applications, we introduce an approach to optimize anthracene-based liquid materials, focussing on enhanced stability, fluorescence quantum yield, colour tunability and processability. Enveloping the anthracene core in low viscosity branched aliphatic chains results in stable, nonvolatile, emissive liquid materials. Up to 96% efficient energy transfer assisted tunable emission is achieved by doping a minute amount of acceptor dye in the solvent-free state. The introduced strategy leading to diverse luminescence colours at a single blue-light excitation can be an innovative replacement for currently used luminescent materials, providing useful continuous emissive layers in developing foldable devices (Fig. 1).



Fig. 1. Liquid anthracene bearing branched alkyl chains (left top), and its blue emitting color under UV irradiation (left down). The luminescent color can be adjusted as a full color (right) by solid phosphor doping into the liquid anthracene.  (2) Directed assembly of optoelectronically active alkyl – π-conjugated liquid molecules by adding n-alkanes or π-conjugated species.<sup>5)</sup>

Supramolecular assembly can yield ordered structures by taking advantage of the cumulative effect of multiple noncovalent interactions between adjacent molecules. The thermodynamic origin of many self-assembled structures in water is the balance between the hydrophilic and hydrophobic segments of the molecule. Here, we show that this approach can be generalized to use solvophobic and solvophilic segments of fully hydrophobic alkylated fullerene molecules.<sup>6</sup> Addition of *n*-alkanes results in their assembly—due to the antipathy of C<sub>60</sub> towards *n*-alkanes into micelles and hexagonally packed gel-fibers containing insulated  $C_{60}$  nanowires (Fig. 2). The addition of pristine  $C_{60}$ instead directs the assembly into lamellar mesophases by increasing the proportion of  $\pi$ -conjugated material in the mixture (Fig. 2). Those assembled structures are confirmed by various analytical techniques including SAXS, SANS, HR-cryo-TEM, POM, rheology and UV-vis absorption spectroscopy. The assembled structures contain a large fraction of optoelectronically active material and exhibit comparably high photoconductivities. This method is shown to be applicable to several alkyl- $\pi$ -conjugated molecules, and can be used to construct organized functional materials with  $\pi$ -conjugated sections.



Fig. 2. Room temperature liquid fullerene- $C_{60}$  bearing branched alkyl chains that can be transformed into micelles and gel fibers by addition of *n*-alkanes as well as forming lamellar mesophase by addition of  $C_{60}$ . Those grown mesoscopic fiber and lamellar structures show photoconductivity.

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## Novel Solar Cell Concept with a Super-wide Response Spectrum Based on III-V Nitride Semiconductors MANA Independent Scientist Liwen SANG



#### 1. Outline of Research

As the famous material system for the solid-state lighting, III-V Nitride semiconductors (GaN, AlN, InN and their ternary and quarternary alloys) also have many advantages for the high-efficiency photoelectricity energy conversion devices since they have the tunable direct bandgaps from the infrared (InN at 0.65 eV) through the visible and the ultraviolet (UV) (GaN at 3.42 eV) to the deep UV region (AlN at 6.2 eV). Compared with Si, GaAs, CuInGaSe, or Ge systems, it is the only semiconductor family that provides the perfect match to the solar spectrum, which opens up an interesting opportunity for high-efficiency full-spectrum photovoltaic applications. The theoretical power conversion efficiency of a four-junction solar cell based on InGaN is expected to be more than 50% according to the balance modeling estimation. However, the progress of the InGaN-based solar cells is still in their infancy (conversion efficiency lower than 4%). The problems lie in two bottlenecks. First, creating high-quality In-rich InGaN alloys (In~40%) to achieve such high conversion efficiency for photovoltaic application remains a challenge. The structural defects such as impuries, V-defects, or phase separation, are usually incorporated as In composition increases. Another bottleneck is the difficulty of p-type doping in In-rich InGaN due to the high n-type background conduction and surface electron accumulation. Therefore, the absorption wavelength of the current InGaNbased solar cells has been concentrated only on the UV region (< 450 nm), leading to an inferior conversion efficiency. To ultimately improve the performance of InGaNbased solar cells, novel concepts are in great demand.

#### 2. Research Activities

We aim to extend the response spectrum of InGaN-based solar cells to the near full-spectrum absorption. Two strategies are proposed to achieve this purpose: intermediate-band solar cells embedded into the wide-bandgap host *p-n* junction for the sub-band absorption and In-rich InGaN thick film grown by high-pressure metal-organic chemical deposition (HPMOCVD).

#### (1) Multi-level intermediate-band solar cells.<sup>1)</sup>

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. From this perspective, the short-circuit current density  $(J_{sc})$  is greatly enhanced compared with that of the single energy gap *p*-*n* junction, while the open-circuit voltage ( $V_{sc}$ ) can be maintained. Theoretically, the IB solar cells provide additional tolerance



Fig. 1. Properties of the InGaN-based IB solar cells.

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. Here, InGaN/GaN quantum dots arrays were used as the IB material, and the sub-band absorptions were successfully realized from both experiment and theoretical calculation. The absorption spectrum was extended from UV to as long as near infrared region (Fig. 1).

#### (2) In-rich InGaN films by HPMOCVD.

From the phase diagram, the only solution to deposit high-quality InGaN thick film without decomposition and less impurities is to grown at high pressures and high temperatures. A high-pressure MOCVD which can go up to 4 atms was designed for the deposition of the In-rich InGaN film. InGaN films with In compositions more than 40% is successfully obtained (Fig. 2).



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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) Hybrid White Light Emitting Diode Based on Silicon Nanocrystals."

A new hybrid device structure was proposed to fabricate white light emitting diodes (WLED). All spectra of white lights were produced by spectral-superposition of red light from the octadecane-terminated silicon nanocrystals (ncSi-OD) layer and blue-green light from the poly-TPD layer in the device active regions of diodes.

The ncSi-OD was prepared by a facile method. Specifically, the tetraethoxysilane was dehydrolyzed into three-valence of Si. Then, the three-valence of Si was disproportionated into zero-valence and four-valence of Si at 1100°C in the inert atmosphere. The silica was removed by fluoride etching. As a result, hydrogen-terminated ncSi was obtained. The surface silicon was replaced by octadecane monolayer by the hydrolyzation of 1-octadecene. Interestingly, ncSi-OD has a large Stokes shift between absorption and emission due to indirect bandgap nature inherited even in nanostructures. By taking advantage of the large Stokes shift featured to the ncSi-OD layer, the photon for EL was generated through the direct injection of electrons and holes into the active device regions from electrodes whereas Förster resonance energy transfer between adjacent emissive layers was suppressed, leading to the successful spectral-superposition for producing the white emission spectra as evidenced in Fig. 1b. As is seen in Fig. 1a, another advantage of our device is a low turn-on voltage (3.5 V) for its operation. The inset of Fig. 1a shows a typical illustration for our prototype of LED device. In the device structure,



Fig. 1. (a) Device current voltage vs voltage plot of the device (inset), and (b) Emission spectra of the devices with and without ncSi layer.

ZnO worked as a good inorganic stable n-type electron injecting layer, and also served as a good hole blocker. The color of the lights emitted from the devices was tuned by film thickness of ncSi-OD layer. The proposed design of devices offers a potential to produce a quasi spectrum of sunlight. It is known that the ncSi is environmental friendly and nontoxic. The present work discloses at the first time WLED with the earth abundant Si avoiding toxic Cd, Pb, As based structure and a simple fabrication process along with a systematic analysis of the device operation.



Fig. 2. (a) Design of SAM microarray with CHO- and NH<sub>2</sub>-capped areas, (b) A process for the ncGe attachment on CHO-capped areas, and (c) Fluorescence microscopic image of the SAM microarray after the attachment of ncGe.

## (2) Monolayer Formation of Luminescent Germanium Nanoparticles on Silica Surface.<sup>2)</sup>

The study reports the monolayer formation of germanium nanoparticles (npGe) on silica substrate. The npGe were prepared by hydride reduction of GeCl<sub>4</sub> with lithium aluminum hydride, and subsequent hydrogermylation of allylamine in the presence of platinum catalyst. The resultant npGe showed the strong blue photoluminescence property. Due to the terminal amine, the npGe was soluble in aqueous buffer solution. To fabricate a monolayer of npGe, its chemical reactivity was studied using a multi functional microarray in which different kinds of siloxane monolayers were periodically aligned on a silica substrate. A fluorescence microscopic image in Fig. 2 provides the direct evidence of successful molecular recognition. In terms of fluorescence observation, the entire surface of the monolayer-covered microsize-domains emits uniformly the blue light. This suggests a high degree of coverage of the luminescent NPs covering over the monolayer regions in the microarray, and implies the non-occurrence of quenching through energy transfer between adjacent NPs.

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## Toward the Development of Future Materials for Fuel Cells MANA Independent Scientist Satoshi TOMINAKA



#### 1. Outline of Research

From the end of 2014, Toyota markets fuel cell cars powered by hydrogen. This is a big step in our society, but does not mean the fuel cell technology is sufficient for creating sustainable society. For example, we need green and sustainable processes for producing hydrogen or alternative fuels, because the current hydrogen supplied for fuel cell cars is produced from natural gas or fossil. Furthermore, the cost of the fuel cells is far more expensive than other power sources for vehicles. This is mainly due to the cost of materials used in the fuel cells, *e.g.*, Pt catalysts and membranes.

For making fuel cells survive in the market, Pt alternative is needed. The alternative has to be composed of abundant elements, and, of course, have comparable or better performance and durability. In details, it needs large surface area, electron conductivity, chemical stability, and catalytic activity. As such materials, I am investigating nanostructured transition metal oxides, *e.g.*, titanium oxides. Here I introduce my recent research works on nano-oxides.

#### 2. Research Activities

# (1) The unique properties of nano Ti<sub>2</sub>O<sub>3</sub> synthesized via a topotactic route.

Reduced titanium oxides are chemically stable and some of them are known to be highly electron conductive. In this light, reduced titanium oxides, mainly  $Ti_4O_7$  and  $Ti_5O_9$  phases, have been used as corrosion-resistant electrodes. They are more stable than precious metals, but it is hard to process these reduced phases, for example, nanosized materials were not obtained. In 2011, we succeeded in the synthesis of nanostructured  $Ti_2O_3$  through topotactic reaction, which enabled reduction of  $TiO_2$  nanoparticles without particle growth.<sup>1-3)</sup> Interestingly, the  $Ti_2O_3$  thus obtained exhibited metallic conduction,<sup>2,3)</sup> which is different from the semiconductive nature of typical  $Ti_2O_3$  synthesized at a high temperature.

Recently, we clarified the origin of the unique properties through the analyses using X-ray pair distribution functions, hard X-ray photoelectron spectroscopy and electron energy loss spectroscopy (Fig. 1): The topotactically formed  $Ti_2O_3$ has lattice strains, which changed the state of conduction band rather than valence band.<sup>4)</sup> The findings confirm that topotactic reactions can create nanomaterials having unique structures and properties that cannot be realized in bulk materials.<sup>4)</sup> Since the reaction rate of topotactic reduction of  $TiO_2$  is in the range of a few hundred nanometers per day, and thus seems not to be suitable for bulk materials, but is



Fig. 1. (a) Atomic structure analyses on Ti<sub>2</sub>O<sub>3</sub> nanoparticles using X-ray PDFs. The experimental plots (blue) were fitted with calculated plots (red). (b) Hard X-ray photoelectron spectra in Ti 2*p* region. The samples are topotactically synthesized Ti<sub>2</sub>O<sub>3</sub> nanoparticles, topotactically synthesized single-crystalline Ti<sub>2</sub>O<sub>3</sub>, bulk Ti<sub>2</sub>O<sub>3</sub>, and a rutile-type TiO<sub>2</sub> single crystal. (c) Electron energy loss spectra in Ti *L*-edge region. Details are reported in reference 4).

sufficient for nanomaterials. We want to emphasize post synthetic treatments of nanomaterials can create new phases having different properties from their bulk phases.

Since the reactions for synthesizing nanomaterials tend to proceed under kinetically controlled conditions, the products may contain nanocrystalline phases and amorphous phases as well as crystalline phases. This often requires pair distribution function analysis for the discussion of their properties, with the presence of additional nanocrystalline or amorphous phases in mind.<sup>4,5)</sup>

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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  $\pi$ -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.<sup>1-4)</sup>

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. We have extended this approach to derive all bulk modes of graphene nanoribbons for arbitrary energy. We derived analytical expressions for these modes and systematically classify them into propagating or evanescent mode. We also demonstrate their uses in efficient electronic transport simulations of graphene-based electronic devices within both the mode-matching method and the Green's function framework. Explicit constructions of Green's functions for infinite and semi-infinite graphene ribbons are presented. In addition, we have analytically studied the quantum interference effect between a vacancy state in graphene and graphene edge states.

#### (2) Boltzmann theory of graphene double-layer systems.<sup>5-7)</sup>

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. 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.

#### (3) Graphene quantum point contacts.<sup>8)</sup>

Electronic localization in narrow graphene constrictions is theoretically studied, and it is found that long-lived (~1 ns) quasibound states (QBSs) can exist in a class of ultrashort graphene quantum point contacts (QPCs). These QBSs are shown to originate from the dispersionless edge states that are characteristic of the electronic structure of generically terminated graphene, in which pseudo-time-reversal symmetry is broken. The QBSs can be regarded as interface states confined between two graphene samples, and their properties can be modified by changing the sizes of the QPC and the interface geometry.

#### (4) 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.<sup>9</sup> We also supported theoretical analysis of the Raman spectroscopy measurements on transition metal dichalcogenides using the density functional theory.<sup>10</sup>

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# Tailored Synthesis of Nanoporous Carbons with<br/>Various ArchitecturesMANA Independent ScientistYusuke YAMAUCHI



#### 1. Outline of Research

Porous carbon materials have unique characteristics, such as a good electrical conductivity, chemical inertness, high surface area, large porosity, and good biocompatibility, thereby showing many potential applications in a wide range of research fields (e.g., adsorption, energy conversion and storage, catalysis, and sensor technology). As demonstrated in many studies, mesoporous materials show excellent performance compared to microporous an materials, because of the less limited diffusion. Using mesopores, especially large-sized mesopores, smooth mass transport can be realized for large reagent molecules. The morphological control is also a critical factor. The spherical morphology attracts sustained research interests especially when the particle size is smaller than 200 nm, because it provides short pathways for mass transport and minimizes the viscous effects. So far, various porous carbon spheres have been prepared using different methods, including hardand soft-templating methods, and a direct polymerization method. However, their pore sizes are still limited to 3 nm. Therefore, such a limitation on the pore size in carbon spheres significantly devalues their practical applications.

#### 2. Research Activities

By using the micelles of a high-molecular-weight block polymer PS-b-PEO as a template, we propose a facile micelle route for the preparation of N-doped mesoporous carbon spheres (NMCS) with large mesopore sizes (up to 16 nm), as shown in Fig. 1.<sup>1)</sup> The key of our synthesis is the use of DA/ PS-b-PEO composite micelles which are stably pre-formed in the reaction solution. Polymerization of the DA molecules and further co-assembly with the PS-b-PEO micelles result in the formation of PDA/PS-b-PEO composite spheres (where polymerized dopamine is abbreviated as PDA). The PS-b-PEO micelles acting as a sacrificial pore-forming agent are removed during the carbonization process, leaving the



Fig. 1. Formation process of the N-doped mesoporous carbon nanospheres (NMCS).

mesopores in the carbon spheres.

The resultant mesoporous carbon spheres are promising catalysts for the oxygen reduction reaction (ORR) and also would show promising applications in large biomolecule adsorption and gene therapy. Toward development of new energy system, researchers are searching for efficient nonprecious metal catalysts or metal-free catalysts as substitution of Pt for the oxygen reduction reaction which is intrinsically sluggish but important in the cathodic reaction. Doping of electron-accepting N atoms in the carbon plane, especially graphitic N and pyridinic N species, is critical for the ORR by imparting higher positive charge density on adjacent carbon atoms and weakening the O-O bond. During the ORR, oxygen can be activated by direct bonding with the lone pair electrons of pyridinic N atoms. And, the graphitic N atoms promote the ORR by electron transfer from the carbon electronic bands to the antibonding orbitals of  $O_2$  and facilitating O<sub>2</sub> dissociation on the adjacent C atoms.

Here we evaluated the ORR activity of non-porous carbon spheres (NCS) and NMCS samples by measuring linear-sweep voltammograms (LSVs) in O<sub>2</sub>-saturated KOH solution using a rotating disk electrode (RDE). To emphasize the importance of our materials, the commercially available Pt catalyst (20 wt% was also measured as a reference). The onset potentials of NCS, NMCS, and Pt/C were -0.15, -0.11, and -0.07 V, respectively, and the limiting currents were 3.14, 5.56, and 5.37 mA/cm<sup>2</sup>, respectively. Clearly, NMCS with large mesopores show a more positive onset potential and a higher diffusion-limited current, compared to NCS with micropores, indicating their better electrocatalytic activity for the ORR.

The improved electrochemical performance of NMCS is a result of their sufficient accessible porous architecture, which can reduce the diffusion resistance and enhance the three-phase boundary of gas, electrolyte, and solid catalyst. Interestingly, NMCS exhibit a similar diffusion-limited current for the ORR compared with Pt/C, although the onset potential is slightly negative. Cyclic voltammography curves of NMCS, performed in N<sub>2</sub>- and O2-saturated KOH solution, presents a distinct cathodic ORR peak at -0.21 V after introducing O<sub>2</sub>, further demonstrating the pronounced electrocatalytic activity of NMCS towards the ORR. The electron transfer number involved in NMCS for the ORR was estimated to be 3.4 from the slope of the Koutecky– Levich plots and was further verified by a rotating ring-disk electrode (RRDE).

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## Development of MSS-Type Nanomechanical Sensors for Real-Time Gas Identification on Mobile Platforms 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)",<sup>1-3)</sup> we are now trying to realize useful nanomechanical sensor systems which can fulfill the practical requirements, such as portability, low-cost, ease of use, in addition to the basic specifications, *e.g.*, high sensitivity and selectivity that will be practically determined with the performance of receptor layers coated on the sensor surfaces.

For gas sensing, one of the most important applications will be non-invasive breath analysis, especially for medical diagnostics. In such an application, the compact sensor systems working on mobile platforms will make a huge impact on medical diagnostics and also on our daily life. So far, we already reported preliminary results of cancer diagnostics using a USB-powered/operated MSS measurement system, demonstrating its high potential as a breath diagnostics tool.<sup>4)</sup>

Since the MSS was verified to fulfill the practical requirements for breath analysis applications, we tried to demonstrate its system-level feasibility as an actual mobile sensing platform.

#### 2. Research Activities

# (1) Demonstration of real-time measurements of breath samples on a mobile phone using a compact module.

Since the MSS platform measures the changes in electrical resistance, a very simple setup is required for basic measurements. To explicitly demonstrate this feature, we assembled a simple read-out module in collaboration with Professor Takatoki Yamamoto from Tokyo Institute for Technology. Fig. 1 shows an example of the real-time



Fig. 1. Demonstration of real-time measurements of breath sample using a polymer-coated MSS chip mounted on a simple readout module which works on a common mobile phone in a plugand-play fashion. measurements using an MSS chip mounted on this module plugged into a mobile phone.

# (2) Real-time gas identification on all-in-one Android platforms with a machine learning algorithm.<sup>5)</sup>

To verify the feasibility of real-time analysis and the identification of gases with the data acquired through a mobile system, we implemented all the components required for quantitative measurements onto a single platform. This unit contains a read-out circuit, a flow chamber, and pumps, in addition to a polymer-coated MSS chip. It transmits data to a consumer mobile tablet where data is displayed and processed in real-time. To achieve real-time processing with the limited computational power of commercial mobile hardware, a machine learning algorithm known as Random Forest was implemented. We demonstrated the real-time identification capability of the device by measuring the vapors of water, ethanol, isopropanol, and ambient air. Fig. 2 shows Android screenshots with real-time prediction scores for each sample gas. The receiver operating characteristic (ROC) scores were also confirmed to have more than 0.99 in each case, demonstrating the high sensitivity and specificity of the present measurement system.<sup>5)</sup>



Fig. 2. Four screenshots of the Google Nexus 7 analyzing different samples. Each sample shows a distinct pattern in its voltage measurements, and the Random Forest prediction is displayed beneath.

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# Tuning Electronic Properties of Atomically ThinNanomaterials: Theoretical PerspectiveICYS-MANA ResearcherSudipta 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. We are planning to investigate the effect of doping, structural and chemical modifications on their electronic, magnetic and transport properties. Furthermore, the hybrid superlattice structures of these layered materials will be studied in search of advanced functionalities. We adopt tight-binding and density functional level of theory along with manybody configuration interaction (CI) numerical method for theoretical explorations.

#### 2. Research Activities

#### (1) Magnetism in Graphene.

Introduction of magnetism in graphene in terms of defects has been gaining interest in recent times, owing to their application possibilities towards spin transport and sensor devices. The fundamental concept of magnetism in graphene bipartite lattice lies in Lieb's theorem, which says: the inequality between two sublattice points, A and B (see Figs. 1a and 1b) introduces net magnetic moment. The graphene unit cell consists of two sublattice points, A and B that prefer opposite spin occupancies, making the over all net magnetization zero (Fig. 1a). Therefore, the vacancy defects can introduce inequality between A and B, making the two-dimensional graphene magnetic.

The formation of zigzag edges, a defect, introduced by finite termination of graphene along a certain crystallographic direction can also introduce net magnetization (Fig. 1c). We observe that, hole doping can make the zigzag edge ribbons magnetic and metallic.<sup>1)</sup> Moreover, in presence of enhanced correlation, the magnetic excitations become more facile.<sup>2)</sup>



Fig. 1. The schematic representation of Lieb's theorem for bipartite lattice (a) and its deviation (b). (c) The schematic representation of CVD growth of graphene with emphasize on the opposite spin localization on either zigzag edges.

The magnetism in graphene can also arise from the grain boundaries, formed during chemical vapor deposition (Fig. 1c). These magnetic grain boundaries induce dispersion less flat bands near Fermi energy, showing higher localization of electrons. These flat bands can be accessed via small doping, leading to enhanced magnetism. Net magnetization in graphene can induce asymmetric spin conduction behavior, which can be exploited for sensor and spin-filtering applications.



Fig. 2. The structure (top) and electronic properties (bottom) of Ca intercalated bilayer graphene (a) and germanene (b). (c) The top view of the geometry with rhombus unit-cell. (d) Brillouin zone of graphene (dashed hexagon) and that of the structure in (c) (solid hexagon). (e) Fermi surface of Ge<sub>6</sub>-Ca-Ge<sub>6</sub>.

#### (2) Intercalated Layered Materials.

The superconductivity of graphite intercalated compounds has been gaining much attention in recent times owing to higher superconducting transition temperature.<sup>3)</sup> However, the origin of superconductivity in this class of materials is still not understood. These studies motivated us to explore the nature of superconductivity in intercalated layered materials and their bilayer sandwich compounds.

The interlayer parabolic bands at G point, which is expected to be responsible for the superconductivity has been observed in case of intercalated graphene, silicene and germanene compounds. In case of Ca atoms sandwiched between bilayer graphene, the experimental observation of this interlayer band indicates the possibility of superconductivity. We too have observed the presence of this interlayer band (at  $\Gamma$  point) in case of bilayer sandwich compounds (Figs. 2a and 2b). The Fermi surface suggests the formation of interlayer parabolic bands (the circular region) at  $\Gamma$  point (Fig. 2e), showing the possibility of superconductivity in atomically thin materials. We are investigating the responsible parameters to tune the superconductivity in layered materials, which will help in fabricating new thin superconductors.

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## Self-Assembled Monolayers Toward New Dynamic and Magnetoresistive RAM ICYS-MANA Researcher Hicham HAMOUDI



#### 1. Outline of Research

The efficiency of the future quantum devices (QD) depends strongly on the homogeneous architecture of the nanocomposite. Systems based on the technology of selfassembled monolayers (SAMs)<sup>11</sup> 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 benzenemetal 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.

A study of the self-assembly of silver atom intercalated 5,50-bis(mercaptomethyl)-2,20-bipyridine DT multilayers on gold was investigated. The bilayer of these SAMs can be obtained starting from the exposure of a DT monolayer to a concentrated silver ion solution. After grafting the silver atoms on the sulfur end group, the incubation of the resulting DT–Ag SAM in a DT solution leads to the formation of a DT–Ag–DT bilayer. This process was extended to make a multilayer structure. The I–V characteristics show a significant bias dependence on the number of the BPD layers and there appears to be a transition from tunneling to a hopping regime when going from the single to the multiple layers.<sup>2</sup>



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



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

#### (2) Freestanding Organometallic Nanosheets.

Using the bottom-up approach (Fig. 1), I have built a new generation of materials for different application such as electronics and energy conversion/storage, these nanosheets was considered as surfaces without bulk "freestanding" organometallic nanosheets<sup>3)</sup> with a nanometer thickness for the mono- and multi- layer sheets (Fig. 2). *(3) Molecular electronics.* 

(3) Molecular electronics.

A bottom-up approach was provided to build a crossbar device using the crosslinked Self-assembled monolayer of the (BPD- Ni<sup>+2</sup>) on gold surface (Fig. 3).<sup>4)</sup> In other hand in a collaboration project with University of Singapore, we have investigated the electrical conductance of tunnel junctions formed by self-assembled monolayers (SAM) of molecules that act as current diodes.<sup>5)</sup>



Fig. 3. The crossbar devices and the molecular diodes projects.

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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. 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.<sup>14</sup>

#### 2. Research Activities

(1) Spatiotemporal control of synergistic hydro-gel disintegration via photoinduced proton transfer.<sup>5)</sup>

Local- and remote-control of gel disintegration was achieved by using photoinduced proton transfer chemistry of photo-acid generator (PAG, Fig. 1). The gels were prepared by simply mixing two polymers via the synergistic interaction of benzoxaborole and diol groups. The *o*-nitrobenzaldehyde (2-NBA) was then loaded into the gel as a PAG. The benzoxaborole-diol interaction was successfully disintegrated upon UV irradiation due to the local pH decrease inside the gel. When the gel was irradiated to a specific gel region, the synergistic interactions were disintegrated only at the exposed region. The ability of the proposed gel-sol transition system via photoinduced proton will be beneficial for not only prompt pH changes within the gel but also the design of predictive and programmable devices for drug delivery.



Fig. 1. Design concept for the local- and remote-control gel disintegration via photoinduced proton transfer chemistry.

(2) Temperature-responsive mixed core nanoparticles consisting of statistical and block copolymers.<sup>6</sup>

A mixed core design approach is achieved using statistical and block copolymers as shown in Fig. 2. To the best of my knowledge, this is the first report that temperature responsive



Fig. 2. Schematic representation of mixed core nanoparticles consisting of self-assembled compatible statistical and block copolymers

block copolymer can recognize its optimum statistical copolymers when they form mixed core nanoparticles. Hydrophobic statistical copolymers were effectively loaded in the micelle cores (the loading capacity 100 %). The polymer density of the shell was also controlled by the mixture ratios of statistical and block copolymers. Moreover, a chimeric core was constructed by mixing statistical copolymers with unique structures, along with the block copolymers. Using this system, nanoparticle properties were easily customized by selecting the specific combination of statistical/block copolymers and were applied in cancer imaging (Fig. 3).



Fig. 3. Cancer imaging by fluorescent mixed nanoparticles.

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# Functionality Driven Application of PorphyrinoidConjugates and NanowiresICYS-MANA ResearcherHuynh Thien NGO



#### 1. Outline of Research

Due to its intrinsic properties, porphyrinoids have been of great interest in a wide range of research area, *e.g.*, catalysis, photodynamic therapy, and molecular electronics, depending on the substitution patterns on the periphery or core of these tetrapyrrolic macrocycles. Recently we focus on the fabrication of nanowires containing porphyrin units. Both unsubstituted porphine and supramolecular multirotaxane systems were designed for this purpose.<sup>1)</sup>



Fig. 1. Porphine nanowire on Ag(111) surface.

#### 2. Research Activities

#### (1) Porphine molecular wire on Ag (111) surface.

In collaboration with Dr. Willi Auwaerter (TU Muenchen), a temperature-induced covalent dehydrogenative coupling between unsubstituted free-base porphine units was achieved leading to dimers, trimers, and larger oligomers directly on a Ag(111) support under ultrahigh-vacuum conditions. The resulting nanostructures range from highly symmetric triply fused porphine dimers to irregular oligomers exceeding 90 porphine units, as controlled by the experimental conditions. STM images reveal different motifs and oligomer lengths. As porphine monomers have no external substitutions, different  $\beta$ - $\beta$ , meso- $\beta$  C-C covalent bonds can be obtained, leading to both symmetric and irregular oligomer patterns (Fig. 1). To realize a linear symmetric nanowire, we prepared two types of porphyrin containing trans-meso-dihalogen moieties (Fig. 2). Br and I are good leaving groups leading to a more trans regiospecific vacant position for C-C bonds. The bulky bis-tertbutylphenyl groups provide sterically hindrance to align the olimerization in one linear direction. The experiments with such monomers are currently under investigation.



Fig. 2. Trans-meso-bromo/iodo porphyrins.



Our recent synthetic efforts have lead to high yielding



Fig. 3. Multirotaxane porphyrinoid conjugates.

metal porphyrinoid hybrids linked by rotaxane units (Fig. 3). Mono-, di- and tetrarotaxane linkers were introduced as linker between different porphyrinoids to control the energy transfer and conductivity. Both conjugate derivatives containing with and without rotaxane linker are under investigation of photophysical properties. We strongly believe that the rotaxane moieties induce extra rigidity in the linker leading to a more efficient energy transfer from the outer corroles to the core porphyrin. We are particularly interested in the exploitation of the "free" space in the macrocycle of the rotaxane. This can act as host for the complexation of metal cations to modify the electronic and magnetic properties. In the near future we devote our attention to the application aspect of such systems in controllable nanowires by external stimuli, e.g. metal center exchange, magnetic field, and UV-Vis irradiation. Using multiprobe AFM, we will investigate the effect of different metal centers containing magnetic moments on the conductivity of the nanowires. Depending on the type of metal ions, and the applied magnetic field we seek to control the conductivity of the nanowires (Fig. 4).



Fig. 4. Conductivity measurements of nanowires with different metal centers and in the presence of magnetic field.

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#### **Development of Optimized Receptor Layers on Gas** Sensing Devices for Non-Invasive Breath Diagnostics **ICYS-MANA Researcher** Kota SHIBA



#### 1. Outline of Research

To reduce increasing medical expenses, we need to address various issues with respect to treatments, prophylaxis and diagnostics. Breath analysis is a potential approach to diagnose diseases in a non-invasive, facile and rapid manner. Therefore, the breath analysis has attracted much attention recently as a next generation diagnostics and the development of proper sensing devices is expected for this purpose. We have developed a sensing platform, a membrane-type surface stress sensor (MSS),<sup>1,2)</sup> which is classified as a nanomechanical sensor and has various merits over conventional sensing devices in terms of sensitivity, stability, portability and so on. Taking advantage of the MSS, a following preliminary result was reported,<sup>3)</sup> head and neck cancer patients were discriminated from healthy persons based only on their exhaled breath. Since there are many different types of other diseases, it is important to further improve sensitivity and selectivity of the MSS in order to realize a super-early stage diagnostics with high accuracy.

#### 2. Research Activities

(1) Development of receptor layer coatings with optimized sensitivity/selectivity by means of functional nanoparticles. In the present study, I plan to utilize well-defined nanoparticles with various surface functionalities as a dopant of receptor layer coatings to optimize sensitivity and selectivity.

Nanomechanical sensors are usually coated with various materials (i.e. receptor layer materials) including selfassembled monolayers (SAMs), DNA/RNA, antigen/ antibody, proteins, polymers and so on depending on target molecules. From a viewpoint of stable and reproducible measurements, it is necessary to design interface between the sensor surface and receptor layer. Thus, the receptor layer materials have to be coated onto the sensor surface under precisely controlled conditions. Taking into account



Fig. 1. The relationship between sensitivity, thickness and Young's modulus of receptor layers.

that thickness and Young's modulus of the coating largely affect sensitivity,<sup>4,5)</sup> many of the conventional receptor layer materials, which form a monolayer coating in principle, are not suitable to achieve high sensitivity. In this sense, polymers are expected as one of the promising materials because they can be readily coated with controlling thickness. According to the previous studies,<sup>4,5)</sup> large sensitivity is given when the thickness is in the range from a few hundred nanometers to a micrometer and Young's modulus is in the range from a few tens of GPa to hundreds of GPa (Fig. 1). However, the Young's modulus in such a range can never be achieved with polymers because Young's modulus of polymers ranges from approx. 0.01 to 10 GPa.

To overcome this difficulty, it would be effective to dope various inorganic-organic hybrid nanoparticles into polymer matrices. I have developed well-defined nanoparticles with various functionalities by means of a microfluidic approach.<sup>6,7)</sup> The concept is shown in Fig. 2. For example, since Young's modulus of titanium oxide is known to be a few hundred GPa, Young's modulus of matrix polymer will be largely increased. In addition, selectivity can be tuned at the same time depending on the composition and surface property of the nanoparticles doped into the matrix polymers. At present, I am trying to optimize sensitivity and selectivity of receptor layers as a first step toward breath diagnostics.



Fig. 2. The concept of the nanoparticle synthesis.

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## Nanomechanical Cleavage of Molybdenum Disulphide Atomic Layers ICYS-MANA Researcher Dai-Ming TANG



#### 1. Outline of Research

Mechanical cleavage technique, also known as the Scotch-tape method, has resulted in the discovery of twodimensional (2D) crystals. It is a rather crude procedure, but, surprisingly, the produced samples demonstrated excellent quality. The simplicity of the Scotch tape method has initiated a booming research on graphene and other 2D materials. However, the atomic processes of the micromechanical cleavage are still poorly understood. How will the atomically thin films behave during the cleavage and under the large bending conditions? Will they bend as a whole plate or will the interlayer sliding occur? Will they lose structural stability under large bending deformation? We design an in situ transmission electron microscopy (TEM) probing technique to investigate the initial stages of the 2D crystal cleavage, which is defined here as the "nanomechanical cleavage", using MoS<sub>2</sub> atomic layers as a model material.<sup>1)</sup>

#### 2. Research Activities

# (1) Nanomechanical cleavage for layer-selective production of 2D crystals.

The MoS<sub>2</sub> crystals (Fig. 1a-c) were loaded in edge-on orientation, as shown in the Schematic (Fig. 1d) and corresponding TEM image (Fig. 1e). A typical sample was about 32 nm in thickness and 380 nm in length. An ultrasharp tungsten tip was manipulated by a piezoelectric motor to approach and contact a MoS<sub>2</sub> single crystal. As shown in the HRTEM image (Fig. 1f), there are pre-existing atomic steps at the crystal surface, therefore the tungsten probe with a tip diameter as small as ~ 10 nm could be manipulated to contact the crystalline edges with a selected number of layers. By using this method, a layer-number-selective cleavage of the MoS<sub>2</sub> atomic layers was realized. Single-, double-, triple-, and multilayers with a thickness of up to 23 atomic layers were successfully cleaved.

(2) Thickness dependent bending behaviors during mechanical cleavage.

The mechanical behaviors of the  $MoS_2$  atomic layers had been closely dependent on the number of layers (thickness) of the flakes. For the 23-layer  $MoS_2$ , we observed the appearance of kinking during bending, which is close to the deformation of the bulk crystals. For the 11-layer  $MoS_2$ and thinner samples, they become highly flexible. Even if the bending radius was as small as 1.3 nm, kinking was absent. The different bending behaviors could be explained by the energies involved in the bending processes. For the double-layer  $MoS_2$ , the interfacial energy dominates and it tends to bend without sliding. In contrast, for the 20 layer- $MoS_2$ , the bending strain energy becomes dominating, and it tends to bend with interlayer sliding. The interfacial energy is a periodic function of the bending slope. Therefore, for



Fig. 1. Nanomechanical cleavage by in situ transmission electron microscope (TEM) probing method.

the thick  $MoS_2$  flakes, during the sliding, when the interlayer sliding distance equals to the lattice constant or any other periodic distance along the sliding direction, the interfacial energy will show local minima. When the energy "valleys" are met, abrupt force drop can be expected, which reflects the formation of kinks.

(3) Cleavage of mono-layer  $MoS_2$  and estimation of the surface energy.

The nanomechanical cleavage process of a monolayer  $MoS_2$  is presented in Fig. 2. After exfoliation, various manipulations could be carried out, such as the bending (a-b), tension (c-d), sliding (e-g) and van der Waals epitaxial stacking (h). The equilibrium shape is determined by the balance between the forces applied by the nanoprobe and the non-covalent dispersion forces in the vicinity of the contact. The surface energy could be calculated by  $\gamma = D/2R^2$ . The specific surface energy of MoS<sub>2</sub> monolayer is calculated to be ~ 0.11 N m<sup>-1</sup>, consistent with the most accurate RPA calculations currently available. Determination of the surface energy is fundamentally important for various processes, such as catalysis, and lubrication.



Fig. 2. Nanomechanical cleavage of a monolayer MoS<sub>2</sub>.

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## N-doped Graphene-Based Electrodes for the Energy Application and their Storage Mechanisms at Atomic Scale

**ICYS-MANA Researcher** 

Xi WANG



#### 1. Outline of Research

The demand for sustainable and clean energy is becoming more and more critical owing to the emergence of electric vehicles and portable electronic devices. Therefore, the search for the next-generation energy-storage materials and studying their underlying storage mechanisms are highly important.<sup>1-3)</sup> Recently, advanced energy storage devices including lithium ion batteries (LIBs) have become one of the most important energy storage devices, which have attracted much attention in the scientific and industrial fields. And there are increasing interests in developing highpower and high-energy anode materials for the next generation high-performance rechargeable LIBs. Among them, N-doped graphenes (GN) are expected to be a good candidate as a promising material, because GN has the intrinsically superior electrical conductivity for fast electron transport, high surface area, open and flexible porous structures available for numerous lithium storage sites and short Li<sup>+</sup> diffusion distances.

Despite of a big success achieved in both experiments and theoretical simulations on GN, there is no direct experimental evidence and fundamental understanding of the lithium storage mechanisms for GN at the atomic scale. Revealing these for GN 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 the contribution of surface capacitive charge to the whole energy, the differences between the material edges and its surface (for both GN and G) in storing mechanism.

#### 2. Research Activities

# (1) Synthesis of GN anode papers and atomic-scale storage mechanisms.

To answer these questions, fabrication of advanced GN anodes and building a GN-based nanobattery are critical. In this study, we firstly created a binder-free N-doped graphene paper anode via a simple solution method<sup>4)</sup> (Fig. 1a), which exhibited both high capacity and ultrafast lithium storage property. Then we constructed a GN-based nano-LIBs device (Fig. 1b) and analyzed its atomistic lithium storage mechanism.

#### (2) DFT calculations.

In order to better understand the differences between GN and G (and, also, between the edge and basal planes) with respect to the storage mechanisms, theoretical calculations (Fig. 1c) were performed. Two structural regions were taken into consideration. Firstly, there exists big discrepancy for G and GN in both structural geometries and bonding configurations. For example, G exhibits a uniform interlayer spacing distance and flat surface. Then we study the effect of GN. There are three main differences for three types of defects. 1) The optimal geometry on lithium adsorption is different. For example, the most stable site of the graphitic N (N1-GN) is on top of a C atom, while Li atom is energetically more favorable to be adsorbed on the center of the defect for the pyrrolic and pyridinic defect structures (N2-GN and N3-GN). In contrast, for Li adsorption in the pure G, Li prefers to occupy the hollow sites of the hexagonal ring, namely, creating only one form-LiC<sub>6</sub>. As a result, the N2-GN and N3-GN (here mainly N2) defects provide a deficiency to gain electron from the Li atom, whereas N1-GN shows a negative effect on Li adsorption. 2) Similarly, the charge transfer from Li is different. Li donates 0.84 |e| charge to GN for N2-GN, much larger than 0.08 |e| to N1-GN. This further demonstrates that pyrrolic N sites show higher efficiency to enhance the interaction between Li atoms and GN surface, leading to ultrafast lithium storage. 3) The pyrrolic N adsorbs Li much easier than graphitic N and pure G due to its larger average adsorption energy for N2-GN. Therefore, the ultra-high capacity of 1193 mAh/g natural for N2-GN system is much larger than for G and N1-GN ones. Above all, after nitrogen doping the number of active binding sites for Li adsorption in the present GN increased, especially for a N2-GN configuration.

three N-substituted configurations on lithium adsorption in



Fig. 1. a) The cross section of GN paper. b) Schematic illustration of an electrochemical device constructed inside the TEM. c-d) Illustrations of G and GN nanosheets for Li-insertion viewed from the edge and basal plan directions.

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



#### 1. Outline of Research

With respect to energy issues of portable electronics and power modules, high-energy high-power electricity storage devices are essential for prolonging service time. Besides, the efficient heat release in electronic components is key in the face of increasing the power consumption of devices. We aim to develop general syntheses for producing highthroughput high-quality nanosheet materials of light elements in boron-carbon-nitrogen system. We further study new energy storage devices based on graphene and carbon nitride nanosheets. We also study the advanced functional composite materials based on novel boron nitride nanosheets for thermal conductive packaging in electronics.

In order to accomplish this purpose, we set up a full set of state-of-the-art instruments for syntheses and characterizations of nanomaterials, such as induction furnace, electrochemical workshop and transmission electron microscope *etc.* We also conducted analyses of electrochemistry, thermology, dielectrics and mechanics with respect to batteries, supercapacitors and composite materials.

#### 2. Research Activities

#### (1) Strutted-Graphene: A New 3D Graphene for High-Power-Density Supercapacitors.<sup>19</sup>

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.



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). 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. 2. (top) In biomass-directed carbothermal reduction, BN nanosheets are spatially converted on the sites where vegetation precursors such as flowers have existed, and they entirely construct and copy the flower-like appearances. The nanosheets are converted at high yield of 20 gram; (bottom) SEM images of BN nanosheets, and a nanosheet taking a truncated hexagon morphology. Its electron diffraction pattern indicates the perfect single crystalline structure of hexagonal boron nitride.

# (2) Massive Synthesis of High-Quality Boron Nitride Nanosheets for Thermoconductive Composites.<sup>2,3)</sup>

We develop an original strategy "biomass-directed onsite synthesis" for the mass production of high-crystalquality BN nanosheets. The strikingly effective, reliable, and high-throughput (dozens of gram) synthesis is directed by diverse biomass sources through the carbothermal reduction of gaseous boron oxide species (Fig. 2). Produced BN nanosheets are single crystalline, laterally large and atomically thin. Additionally, they assemble themselves to the same macroscopical shapes peculiar to original biomasses. The nanosheets were further utilized for making thermoconductive and electrically insulating epoxy/BN composites with a 14-fold increase in thermal conductivity, which are envisaged to be particularly valuable for future high-performance electronic packaging materials.

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# Towards Metal-Organic Framework Nanoarchitectonics:Fundamentals of Synthesis and DesignICYS-MANA ResearcherHamish Hei-Man YEUNG



#### 1. Outline of Research

From their humble beginnings in the 1990's as Chemistry's molecular equivalent of Tinkertoy<sup>®</sup>, Metal-Organic Frameworks, MOFs, now find themselves investigated for several advanced applications. These include, in addition to conventional gas storage and separations, applications that exploit flexibility, tunability and synergy between "organic" and "inorganic" components in these unique materials. Yet, in order to make the difficult transition from interesting materials to functional materials, a deeper understanding of MOF formation and their post-synthetic transformations is required, which will result in greater control over device fabrication and enable the targeted design of new MOFs for specific applications.<sup>1)</sup>

#### 2. Research Activities

#### (1) In-situ diffraction of MOF crystallization.

The lithium tartrates - lightweight analogues of Rochelle Salt, the first ferroelectric – are a unique model case for investigating structures, energetics and formation behaviour of MOFs. The crystal structures of eight anhydrous polymorphs are known, for which the relative formation energies have been calculated and related to various structural features and synthesis conditions via ex-situ experiments.<sup>2)</sup> By combining new *in-situ* synchrotron X-ray diffraction measurements<sup>3</sup>) with previous structural and thermodynamic information, we have now revealed more detailed insight than ever before into the formation of lithium tartrates as a function of reaction temperature, time and solvent. In monitoring the reaction evolution in real time, we have not only uncovered a wide range of kinetic and phase selection behaviours (Fig. 1), but we have observed new crystalline reaction intermediates. This



Fig. 1. Conversion from the metastable lithium tartrate 7 to thermodynamic 6 measured by *in-situ* synchrotron X-ray diffraction.

suggests a new formation mechanism for these intriguing materials, which paves the way for advances in MOF device fabrication.<sup>4)</sup>

#### (2) Topotactic dehydration of a dense MOF.

The crystal engineering approach to topochemical reactions has traditionally been dominated by non-covalent forces, which can accommodate the crystal strain accompanying bond breaking and formation. Despite their relative rigidity, however, coordination bonds impart extra stability to organic molecules, allowing access to more demanding conditions, such as higher temperatures and pressures, as well as giving excellent control over molecular conformations.<sup>2)</sup> This stability is exploited in lithium l-malate, which undergoes topotactic dehydration when heated to 280 °C, forming a phase containing the unsaturated fumarate ligand, in which the original 3-D framework remains intact. Insight into this unusual transformation has been obtained by single crystal X-ray diffraction, MAS-NMR, *in-situ* powder X-ray diffraction (Fig. 2) and DFT calculations.<sup>5)</sup>



Fig. 2. Variable-temperature powder X-ray diffraction following the topotactic dehydration of lithium l-malate during heating.

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