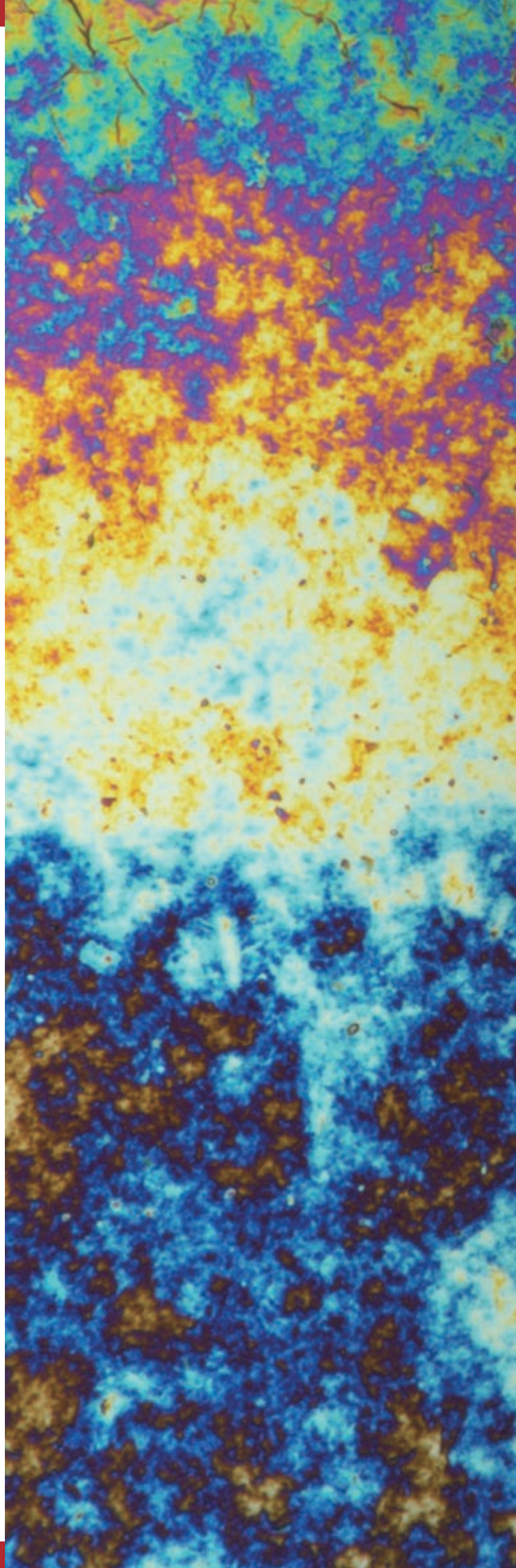
Nano Revolution
for the Future

MANA DIGEST 2019



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

Preface:

Takayoshi Sasaki
MANA Director
NIMS

MANA's New Mission

The International Center for Materials Nanoarchitectonics (WPI-MANA) was established at NIMS in 2007 in the framework of the World Premier International Research Center Initiative (WPI), which is sponsored by Japan's Ministry of Education, Culture, Sports, Science and Technology (MEXT). Thanks to the great effort and support of many people over 10 years, we are proud that WPI-MANA has grown into a representative international research center in the fields of nanotechnology and material science, both in name and reality. It is needless to say that for the sustainable development of human society, innovative technologies that are based on discovery and creation of appropriate materials play a crucial role to solve various problems. In recent years, nanotechnology has made astonishing progress and became a modern pillar of materials discovery and development. WPI-MANA is pursuing innovation on the basis of our concept of "nanoarchitectonics," where new materials and functions are created by rationally integrating and joining nanoscale parts. "Nanoarchitectonics" has now grown into a concept that is accepted around the world.

As the 10 year WPI funding has ended, WPI-MANA is strongly required to grow and develop further, and to continue world leading research activities as an international hub institute for nanotechnology research. We are well aware of it and will continue to deepen and pursue our "nanoarchitectonics." In connection with it, we are striving for new horizons such as heterojunction of dissimilar materials, close cooperation between theory and experiment, and challenge of large scale and complex systems. All of these are considered to be key research for our "nanoarchitectonics" to demonstrate its real value. We look forward to your continued support for further development of WPI-MANA.

wpi

MANA
Nano Revolution
for the Future

NIMS

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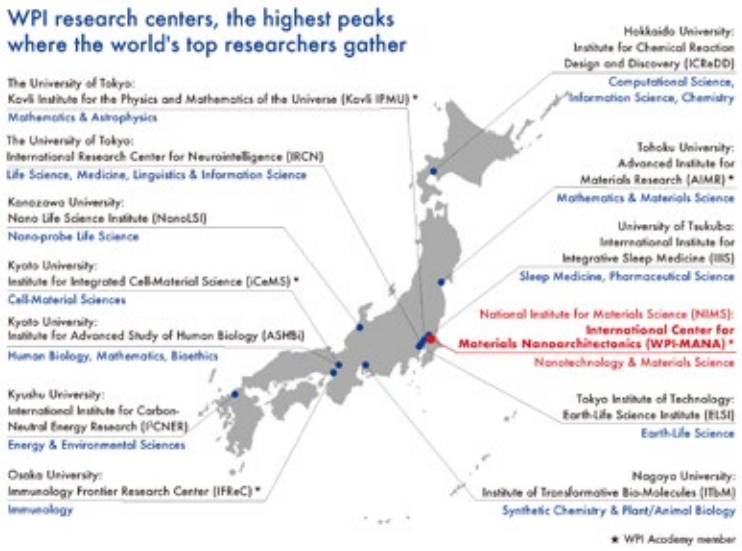
Cover Nano-Art:
Graphene Micro Universe by Dr. Gaku Imamura (MANA).
Optical microscope image of graphene oxide coated on a silicon substrate.

WPI and MANA:

• World Premier International Research Center Initiative (WPI):

In recent years, a competitive search for the most talented minds has been advancing rapidly around the world. This trend in human resources is known as "brain circulation." WPI centers serve as models of research institutes in Japan, and are expected to bring innovations in science and technology.



• MANA Top Management, Workforce and Advisors:

Top Management

Takayoshi Sasaki
Director

Tomonobu Nakayama
Deptuy Director, Administrative Director

Yutaka Wakayama
Deptuy Director

Workforce

(as of October 2019)

	Number	Non-Japanese	Females
PIs	23	9	2
Group Leaders	11	1	0
Associate PIs	1	0	0
Faculty Scientists	67	10	9
Postdoctoral Researchers	63	46	13
Junior Researchers	54	38	12
Administrative and Technical Staff	61	2	46
Total	**280**	**106**	**82**

Executive Advisors

M. Aono
Former Director
International Center for Materials Nanoarchitectonics

Y. Bando
Former COO
International Center for Materials Nanoarchitectonics

Advisors

J.M. Lehn
Professor, University of Strasbourg, Nobel Laureate in Chemistry (1987)

C.N.R. Rao
Honorary President, Javaharlal Nehru Center for Advanced Scientific Research

T. Kishi
Former President, National Institute for Materials Science

H. Fukuyama
Director General
Research Institute for Science and Technology, Tokyo University of Science

MANA, the WPI Research Center at NIMS:

● What is MANA?

The International Center for Materials Nanoarchitectonics (WPI-MANA) was founded in October 2007 as one of the original five centers under the World Permier International research Center Initiative (WPI) of Japan's Ministry of Education, Culture, Sports, Science and Technology (MEXT).

MANA's Vision

Toward a better global future:
Pioneering a new paradigm in materials development
on the basis of "nanoarchitectonics"

MANA's Mission

- Develop groundbreaking new materials on the basis of "nanoarchitectonics"
- Create a "melting pot" where top-level researchers gather from around the world
- Foster young scientists who battle to achieve innovative research
- Construct a worldwide network of nanotechnology research centers

● What is Nanoarchitectonics?

The New Paradigm of Nanotechnology

Nanotechnology plays an extremely important role in the development of new materials. Yet, nanotechnology tends to be misunderstood as a simple extension of the conventional microtechnology that has demonstrated great effectiveness in micro-fabrication of semiconductor devices–in other words, as a refinement of microtechnology. In fact, however, nanotechnology and microtechnology are qualitatively different. At WPI-MANA, we call the new paradigm of nanotechnology, which correctly recognizes this qualitative difference, "Nanoarchitectonics."

Four key points of Nanoarchitectonics

1 "Unreliability-tolerant reliability"
2 "From nano-functionality to nanosystem-functionality"
3 "More is different"
4 "Truth can be described with plain words"

Grand Challenges

- Nano perceptive system
- Nanoarchitectonic artificial brain
- Room-temperature superconductivity
- Practical artificial photosynthesis

Internationalization of MANA:

● MANA Satellite Laboratories:

To implement the internationalization of our research environment, WPI-MANA invited prominent researchers as Satellite PIs and established satellite laboratories at each research institute. From 23 Principal Investigators, 7 are affiliated with satellite institutions. Satellite provide support for joint research in fields that can't be covered by NIMS alone. Satellite PIs act as mentors to young researchers at MANA.

● Melting Pot Environment:

WPI-MANA provides a "Melting Pot Environment" where many researchers from different research fields, cultures and nationalities gather. This approach fosters a creative research environment by removing various barriers among researchers. Free communication and exchange of opinions cultivates ideas of interdisciplinary research. Approximately half of the researchers enrolled in WPI-MANA are foreign nationals. WPI-MANA provides a variety of support for them. The administrative office is composed only of staff who can speak English, and all necessary procedures can be done in English.

Internationalization of MANA:

● International Nanotechnology Research Network:

MANA signs Memoranda of Understanding (MOUs) with universities and research institutes around the globe in order to promote the creation of an international nanotechnology research network by way of joint research projects. In 2019, ten MOU agreements have been signed.

1	University of Strasbourg, CNRS, **France** **(MANA Satellite)** Signed on January 21, 2019
2	Commonwealth Scientific and Industrial Research Organization (CSIRO), **Australia** Signed on March 19, 2019
3	Qatar Environmental & Energy Research Institute (QEERI), **Qatar** Signed on May 8, 2019
4	University of Naples Federico II (+INFN +CNR +KEK), **Italy** Signed on June 13, 2019
5	National Chiao Tung University (NCTU), **Taiwan** Signed on July 2, 2019
6	Catalan Institute of Nanoscience and Nanotechnology (ICN2), **Spain** Signed on October 16, 2019
7	National Cheng Kung University (NCKU), **Taiwan** Signed on October 30, 2019
8	Sydney Nano Institute, University of Sydney, **Australia** Signed on November 12, 2019
9	Nepal Academy of Science and Technology (NAST), **Nepal** Signed on December 16, 2019
10	Faculty of Chemical Technology, Pardubice University, **Czech Republic** Signed on December 18, 2019

● MANA E-Bulletin:

Since December 2017, MANA releases its own web-based media "MANA E-Bulletin," which contains a feature article with a prominent researcher and research highlights & news from MANA. E-Bulletin is also available as a hard-copy publication. In 2019, three issues of MANA E-Bulletin have been released.

No. 6
(March 2019)

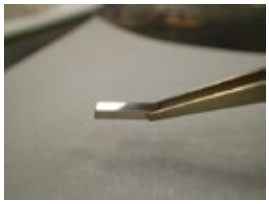
No. 7
(June 2019)

No. 8
(November 2019)

Press Releases from MANA:

Discovery of Significant Increase in Thermoelectric Performance in Ferromagnetic Materials – New Approach to Increasing Thermoelectric Performance at Near Room Temperature –

March 5, 2019 *Paper:* doi: 10.1126/sciadv.aat5935

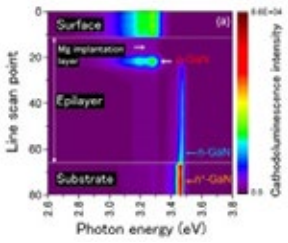


NIMS and Hitachi Ltd., have jointly discovered that the thermoelectric performance of a weakly ferromagnetic alloy dramatically increases in a wide range of temperatures near the ferromagnetic transition temperature (Tc) at which they become non-magnetic. This study demonstrated for the first time that the thermoelectric performance of ferromagnetic materials substantially increases in response to changes in magnetic properties and may serve as a new approach to designing highly efficient thermoelectric materials.

Researchers from MANA: N. Tsujii, T. Mori

Nanoscale Visualization of the Distribution and Optical Behavior of dopant in GaN – Significant Advances in the Understanding of P-Type GaN Semiconductor Formation Mechanisms and Techniques Enabling Mass Production of GaN Devices –

May 22, 2019 *Paper:* doi: 10.7567/1882-0786/ab14cb

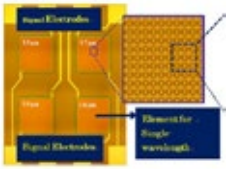


In Gallium Nitride (GaN) implanted with a small amount of magnesium (Mg), NIMS succeeded for the first time in visualizing the distribution and optical behavior of the implanted Mg at the nanoscale which may help in improving electrical performance of GaN based devices. Some of the mechanisms by which introduced Mg ions convert GaN into a p-type semiconductor are also revealed. These findings may significantly expedite the identification of optimum conditions for Mg implantation vital to the mass production of GaN power devices.

Researchers from MANA: J. Chen, W. Yi, T. Kimura, T. Sekiguchi

A Spectroscopic Infrared Sensor with World-Class Wavelength Resolution – Realizing 50nm Resolution and ±1° Sensing Angle Towards the Development of Advanced Temperature and Position Sensors –

August 26, 2019 *Paper:* doi: 10.1002/advs.201900579

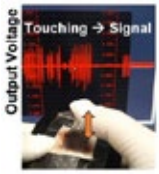


NIMS has developed a multi-wavelength infrared sensor capable of discriminating between thermal radiation of different wavelengths radiating in specific direction. With a wavelength resolution of 50 nm and a sensing angle of ±1°, this sensor may be used to remotely measure the temperatures of objects and analyze their thermal states even when their thermal radiation properties are unknown. This technology may also be applicable to the development of high-accuracy position sensors and gas sensors.

Researchers from MANA: T.D. Dao, S. Ishii, A.T. Doan, T. Nabatame, T. Nagao

Development of a Stretchable Vibration-Powered Device Using a Liquid Electret – Towards Healthcare-Applicable Heartbeat and Pulse Sensors –

September 30, 2019 *Paper:* doi: 10.1038/s41467-019-12249-8



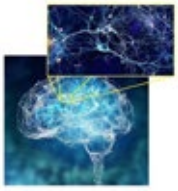
NIMS and AIST developed a liquid electret material capable of semi-permanently retaining static electricity. They subsequently combined this material with soft electrodes to create the first bendable, stretchable vibration-powered device in the world. Because this device is highly deformable and capable of converting very subtle vibrations into electrical signals, it may be applicable to the development of healthcare-devices, such as self-powered heartbeat and pulse sensors.

Researchers from MANA: K. Nagura, S. Ishihara,T. Nakanishi

Press Releases from MANA:

Brain-like Functions Emerging in a Metallic Nanowire Network – Emerging Fluctuation-based functionalities are Expected to Open a Way to Novel Memory Device Technology –

November 11, 2019 *Paper:* doi: 10.1038/s41598-019-51330-6

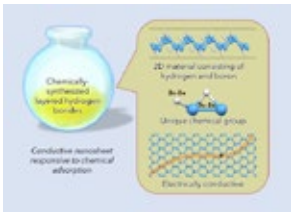


An international joint research team led by NIMS succeeded in fabricating a neuromorphic network composed of numerous metallic nanowires. Using this network, the team was able to generate electrical characteristics similar to those associated with higher order brain functions unique to humans, such as memorization, learning, forgetting, becoming alert and returning to calm. The team then clarified the mechanisms that induced these electrical characteristics.

Researchers from MANA: A. Diaz-Alvarez, R. Higuchi, Y. Shingaya, J.K. Gimzewski, T. Nakayama

Development of a Novel Nanosheet with Adjustable Electrical Conductivity – Unique Hydrogen-Boron Structure Capable of Adsorbing Organic Molecules May Be Applicable to the Development of Molecular Sensors and Catalysts –

December 10, 2019 *Paper:* doi: 10.1016/j.chempr.2019.11.006

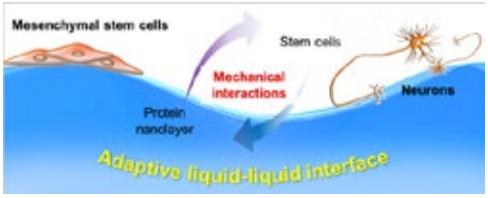


A research team led by NIMS and University of Tsukuba developed a new nanosheet composed exclusively of boron and hydrogen. This research team and JASRI then discovered that the nanosheet contains unique hydrogen atom arrangements which promote molecular adsorption on its surfaces, significantly influencing the electrical conductivity of the nanosheet. This lightweight, flexible nanosheet with adjustable electrical conductivity may apply to the development of wearable electronic devices and sensors with novel working mechanisms.

Researchers from MANA: S.Tominaka, K.Kawakami

Differentiation of Stem Cell into Neurons on an Interfacial Protein Nanolayer – Deformable and Dynamic Scaffolds Can Offer an Alternative Approach in Regenerative Medicine to Regulate Stem Cell Differentiation without Expensive Reagents –

December 10, 2019 *Paper:* doi: 10.1002/adma.201905942

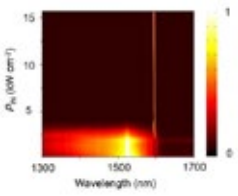


NIMS has succeeded in induction of stem cell differentation into neurons on the surface of a protein nanolayer formed between two immiscible liquids (water and a perfluorocarbon liquid) without using expensive reagents. This technique is capable of regulating stem cell differentiation at low cost and may be valuable in regenerative medicine and other related fields.

Researchers from MANA: X.F. Jia, K. Minami, K. Uto, A.C. Chang, J.P. Hill, J. Nakanishi, K. Ariga

Discovery of a New Lasing Phenomenon in Honeycomb Structure – Topology Induces Wave Confinement, Shining Light to the Development of Groundbreaking Microlaser Technologies –

December 17, 2019 *Paper:* doi: 10.1038/s41565-019-0584-x



A NIMS research team discovered a novel wave confinement induced by the topological property of honeycomb photonic crystals, and succeeded in fabricating a microlaser with excellent directionality. As the key element for innovative technologies in communications, sensors, material processing and DNA manipulation, the high-quality microlaser is expected to be useful for a broad scope of applications.

Researchers from MANA: X.X. Wang, X. Hu

Outreach Activities and Events:

● Kagaku-zanmai Event (December 2018, WPI event)

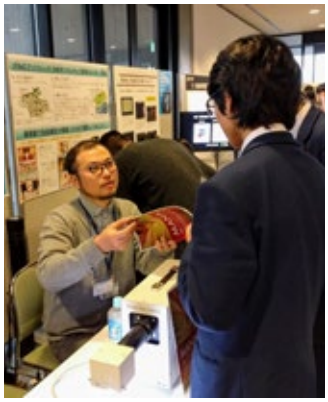
Kagaku-zanmai (Everything Science) is an event where all the SSH high schools and University students in the Chubu-area gather once a year to present their research topics and poster presentations. WPI centers including MANA took part at the event at Nagoya University with their own booths.

● The 7th WPI Science Symposium (December 2018, WPI event)

The WPI Science Symposium mainly focuses on the presentation of the achievements of the WPI centers to the young generation and to general people. The 7th WPI Science Symposium was held at Nagoya University after the Kagaku-zanmai event.

● Science Experiment Class at Primary School (January 2019)

The Smart Polymer Group of MANA supported by the MANA Outreach Team held a Science Experiment Class at a Primary School at Hitachinaka, Ibaraki. The “Smart Polymer Rangers” helped the attending primary school, junior high school and high school students to discover the Smart Polymer's outstanding functions that will be used in the medical field.



Kagaku-zanmai Event

WPI Science Symposium

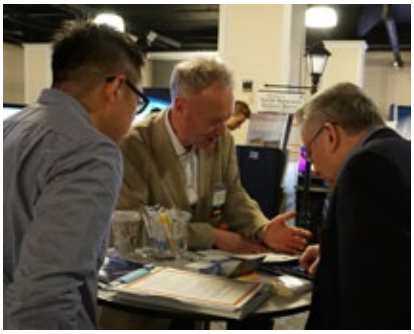
Science Experiment Class

● AAAS Annual Meeting (February 2019, WPI event)

MANA participated in the WPI booth at the at AAAS Annual Meeting 2019 held at Washington DC, USA.

● NIMS Open House (April 2019)

Recently, the yearly NIMS Open House event gathers more and more visitors each year.The MANA Outreach team had an experimental booth at the NIMS Namiki site to present some of the latest research findings including Dr. Ishii’s room temperature vaporing system and Dr. Ebara’s “Smart Polymer Ranger’s” science show.



AAAS

AAAS

NIMS Open House

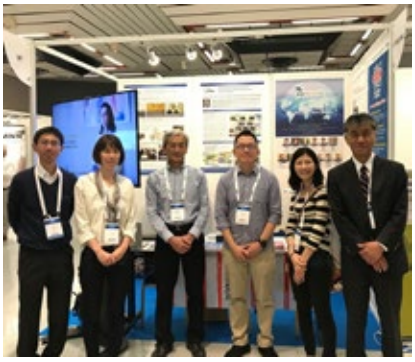
Outreach Activities and Events:

● EMRS Spring Meeting (May 2019, WPI event)

Material Science related WPI research centers, including MANA, attended the EMRS Spring Meeting in Nice, France, with their own booth to recruit young and talented scientists in Europe.

● Super Science High School National Convention (August 2019)

Super Science High School (SSH) is a system established by MEXT for high schools that focus their education on science and mathematics. SSH is supported by the Japan Science and Technology Agency (JSTA). MANA attended the Super Science High School National Convention 2019 in Kobe to present eye-catching research results to talented young high school students.



EMRS Spring Meeting

EMRS Spring Meeting

Super Science High School National Convention

● Tsukuba Science Festival (November 2019)

The Tsukuba municipal government organizes the yearly Tsukuba Science Festival to present science to the citizens. The Smart Polymer Group of MANA supported by the MANA Outreach Team presented the Smart Polymer Rangers' experimental quiz show at the festival at the Tsukuba Capio Hall.

● MANA Crowd Funding Projects Science Café (December 2019, WPI Fund Raising Activity)

In connection with the Crowd Funding Projects, MANA organized a Science Café at Tsukuba Bivi, the commercial building located in close to Tsukuba train station. The two project leaders, Dr. Ishii and Dr. Ebara, informed the supporters about the topic and ongoing progress of the MANA Crowd Funding Projects.

Tsukuba Science Festival

Science Café (Dr. Ishii)

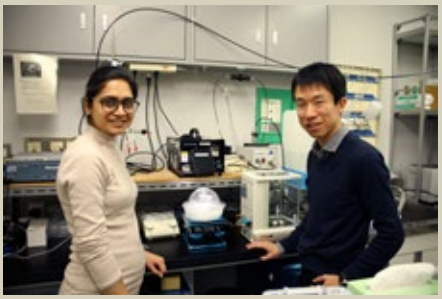
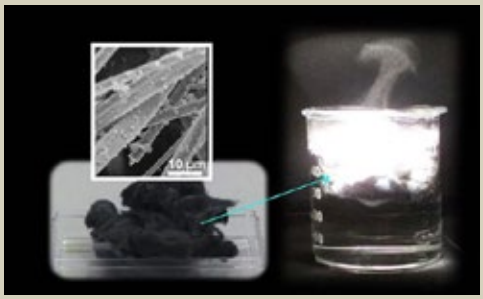
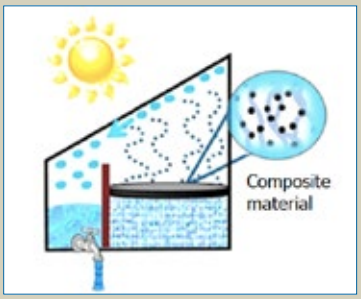
Science Café (Dr. Ebara)

Outreach Activities and Events:

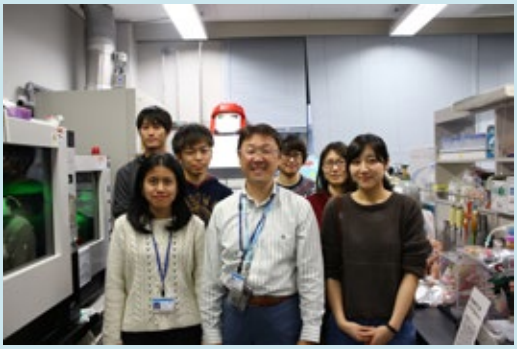
academist

Within the WPI Fund Raising Activity, MANA has successfully challenged two Crowd Funding Projects in 2019 on the academic crowd funding service platform "academist." https://academist-cf.com

MANA Crowd Funding Project #1 (2019):
Project title: Demonstration of highly efficient solar water distillation system
Researchers: Satoshi Ishii (Senior Researcher), Manpreet Kaur (Junior Researcher)
National Institute for Materials Science (NIMS), International Center for Materials Nanoarchitectonics (WPI-MANA)
The funding target has been reached in March 2019.
Target Amount: 400,000 JPY Pledged: 631,600 JPY (157%)
Project Description: We have succeeded in fabricating highly efficient sunlight-driven water evaporating material which is consisted of titanium nitride (TiN) nanoparticles as sunlight absorbers and ceramic wool for sucking water by capillary force. Since this composite material is simple and easy to handle, it has potentials to desalinate sea water in areas where people suffer from water shortage and to supply water in devastated areas. A material is valuable when it is used in real life. In the current project, we intend to bring our research result to practical usage.

MANA Crowd Funding Project #2 (2019):
Project title: Wearable Artificial Kidney ~ Development of Smart Nanofiber Meshes to Remove Uremic Toxins ~
Researcher: Mitsuhiro Ebara (Group Leader)
National Institute for Materials Science (NIMS), International Center for Materials Nanoarchitectonics (WPI-MANA)
The funding target has been reached in July 2019.
Target Amount: 800,000 JPY Pledged: 948,920 JPY (118%)
Project Description: Although the most common treatment for kidney failure is hemodialysis, it requires water, electricity and careful maintenance, and is therefore restricted in developing countries and during natural disasters. Throughout this crowd funding, we would like to develop a way of removing toxins and waste from blood using a cheap easy-to-produce nanofiber mesh. The mesh could be incorporated into a blood purification product small enough to be worn on a patent's arm, reducing the need for expensive, time-consuming dialysis.



Outreach Activities and Events:

● Zhong Lin Wang (MANA Satellite PI) wins the 2019 Albert Einstein World Award of Science

The prestigious Albert Einstein World Award of Science issued by the World Cultural Council (WCC) has been given for Prof. Zhong Lin Wang's pioneering and seminal contributions to the discovery, innovation and implementation of nanogenerators and self-powered systems. These innovations enable unprecedented new technologies for harvesting energy from the environment and biological systems, with applications in personal electronics, sensor networks, biomedical and healthcare devices, and environmental monitoring. The jury also acknowledged the significant impact of his discoveries and breakthroughs, which have already inspired worldwide efforts in academia and industry towards a wide range of technological applications that will be of great benefit to humankind and the sustainable development of our society. The award ceremony has been held in October 2019 at the University of Tsukuba, Japan, in the framework of the Tsukuba Conference.

● Katsuhiko Ariga (MANA PI) wins the "40th Langmuir Lectureship Award"

Katsuhiko Ariga is the first Japanese to receive the Langmuir Lectureship Award issued by Langmuir (ACS Publications, American Chemical Society) and the ACS Division of Colloid & Surface Chemistry. Dr. Ariga gave a talk at a dedicated symposium and award ceremony organized by the ACS Division of Colloid & Surface Chemistry at the 2019 Fall ACS National Meeting in San Diego, California.

● Tomonobu Nakayama (MANA Deputy Director) elected as JSAP Fellow 2019

Tomonobu Nakayama was selected as the Fellow of the Japan Society for Applied Physics (JSAP). The award title is "Exploration of functionality based on atom/molecule manipulations and development of nano characterization tools" and the ceremony was held at the 80th JSAP Autumn Meeting at Hokkaido University in September 2019.JSAP has established the fellow commendation system to recognize researchers who have made significant contributions to the development of applied physics through ongoing activities.

● Genki Yoshikawa (MANA Group Leader) received the Seiyama Prize

Genki Yoshikawa, Group Leader of Nanomechanical Sensing Group, received the Seiyama Prize of the Japan Association of Chemical Sensors for "Development of Membrane-type Surface stress Sensor (MSS) and related technology system."

● Naoyuki Kawamoto, Principal Researcher of Nanotubes Group, received the "Encouraging Prize" of the Japanese Society of Microscopy

Naoyuki Kawamoto, received the "Encouraging Prize" of the Japanese Society of Microscopy for the "Development of STEM-Based Thermal Analytical Microscopy."

Katsuhiko Ariga
(Langmuir Lectureship Award)

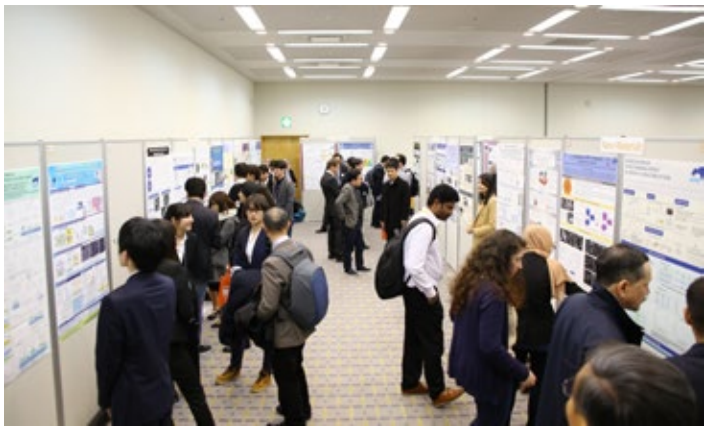
Tomonobu Nakayama
(JSAP Fellow 2019)

Genki Yoshikawa
(Seiyama Prize)

Conferences:

● MANA International Symposium (March 2019):

The 12th MANA International Symposium 2019 jointly with ICYS "Toward Perceptive Nanomaterials, Devices and Systems" was held at Epochal Tsukuba in Tsukuba City over a 3-day period on March 4-6, 2019. The MANA International Symposium is held every year to present MANA's research achievements to the domestic and international scientific community and to discuss the current status and the future perspective of materials science and technology based on state-of-the-art nanotechnology.



The Symposium featured three keynote lectures given by two MANA satellite PIs, Prof. Gero Decher from University of Strasbourg, France and Prof. Thomas Mallouk from University of Pennsylvania, USA, and by Prof. Yoshihiro Iwasa from University of Tokyo. The symposium with 336 participants from 12 countries consisted of 11 invited speakers from inside and outside Japan, 10 speakers from MANA and 129 poster presentations.

Prof. Takayoshi Sasaki
(Director of MANA, NIMS)

Prof. Gero Decher
(Univ. of Strasbourg, France)

Prof. Thomas Mallouk
(Univ. of Pennsylvania, USA)

Prof. Yoshihiro Iwasa
(University of Tokyo)

Conferences:

● The 3rd International Symposium on Nanoarchitectonics for Mechanobiology (March 2019)

The 3rd International Symposium on Nanoarchitectonics for Mechanobiology with 118 participants was held at the auditorium in the WPI-MANA building over 2 days on March 7-8, 2019. Following the first two symposia in 2016 and 2017, the purpose of the 3rd symposium was to pursue new mechanobiology in conceptual similarity between mechanobiology and MANA's concept "nanoarchitecics." We hope that this symposium helped to accelerate fusion research between biology and materials science. The 4th symposium is planned to be held in Seattle, USA.

● The 2nd International Symposium on Chemistry of Nanomaterials (March 2019)

The 2nd International Symposium on Chemistry of Nanomaterials with 105 participants was held at the auditorium in the WPI-MANA building on March 28-29, 2019. In recent years, the development of new nanomaterials, in particular 2D nanosheets, and the discovery of new functions have been remarkable, and the concept of nanoarchitectonics has been used to construct nanostructures with various new functionalities. The first symposium was successfully held in February 2017 between the three institutes as VISTEC (Thailand), Ewha Women's University (South Korea) and MANA, in Vidyasirimedhi Science and Technology Institute (VISTEC), Thailand. The 3rd symposium is planned to be held in South Korea.

International Symposium
on Nanoarchitectonics for Mechanobiology

International Symposium
on Chemistry of Nanomaterials

● The 2nd International Workshop TOPOLOGY (June 2019)

The 2nd International Workshop “Topology: the New Horizon of Materials Science and Nanophotonics” with 141 participants was held at the auditorium in the WPI-MANA building over two days on June 12-13, 2019. Recent years have seen a surge of research interest on topological states in electronic systems and related quantum matters. The concept of topology has been extended to various systems and physical waves, and the realization of new characteristics, new devices and innovative functions are strongly expected.

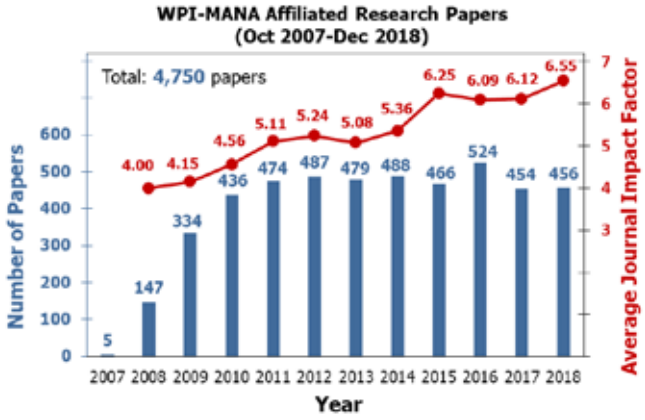
Prof. F. Duncan Haldane
(Novel Laureate, Princeton Univ.)

Prof. Q. Niu
(University of Texas)

Prof. Xiao Hu
(MANA PI, NIMS)

MANA's Research Results:

● MANA Affiliated Papers (Oct 2007 – Dec 2018):



- **4,750** Research papers
- Average journal impact factor: **6.55** (in 2018)

- Internationally co-authored MANA papers: **70.6**% (in 2018) and **50.9**% (in average)

In total, 4,750 MANA affiliated papers have been published. The average impact factor* of the journals in which 456 papers were published in 2018 was 6.55 which reflects the high quality of research results at WPI-MANA.

* Impact Factor: Based on Web of Science data base, the degree of influence is measured numerically and expressed based on the frequency of citation of published articles in scholary journals.

Internationally co-authored papers released by WPI-MANA has been increasing each year. Since 2015, more than half of the total number of papers have been internationally co-authored. In 2018, the proportion of internationally co-authored papers reached 70.6% and this number represents the internationality of WPI-MANA.

Among the 4,750 papers published by WPI-MANA in 2007-2018, **163 papers** are Highly Cited Papers (**top 1% papers**) based on Web of Science database (as of December 2019).

● MANA Patents (Oct 2007 – Dec 2018):

In 2018, the number of **patents** acquired by WPI-MANA reached **768** (578 domestic, 190 international). This shows the breadth of potential in nanomaterials, and the WPI-MANA's proactive approach to the development of new technology, spanning from basic research to applied research.

MANA's Research Results:

• Highly Cited Researchers 2019 from MANA:

Katsuhiko Ariga
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Yoshio Bando
Executive Advisor
Materials Science

Dmitri Golberg
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Materials Science

Jonathan P. Hill
Chief Researcher
Cross-Field

Thomas E. Mallouk
MANA PI
Cross-Field

Zhong Lin Wang
MANA PI
Materials Science

Yusuke Yamauchi
MANA PI
Chemistry

Jinhua Ye
MANA PI
Materials Science, Chemistry

• MANA Papers 2019 published in High-Impact Factor Journals:

Authors with MANA Affiliation

Impact Factor 2018: **43.070**	B. Hinterleitner, I. Knapp, M. Poneder, Y. Shi, H. Müller, G. Eguchi, C. Eisenmenger-Sittner, M. Stöger-Pollach, Y. Kakefuda, N. Kawamoto, Q. Guo, T. Baba, T. Mori, S. Ullah, X.Q. Chen, E. Bauer, *Thermoelectric performance of a metastable thin-film Heusler alloy*, **Nature 576**, 85 (2019). doi: 10.1038/s41586-019-1751-9
Impact Factor 2018: **43.070**	Y. Yamashita, J. Tsurumi, M. Ohno, R. Fujimoto, S. Kumagai, T. Kurosawa, T. Okamoto, J. Takeya, S. Watanhabe, *Efficient molecular doping of polymeric semiconductors driven by anion exchange*, **Nature 572**(7771), 634 (2019). doi: 10.1038/s41586-019-1504-9
Impact Factor 2018: **41.037**	Y.B. Yang, X.D. Yang, L. Liang, Y.Y. Gao, H.Y. Cheng, X.M. Li, M.C. Zou, A.Y. Cao, R.Z. Ma, Q. Yuan, X.F. Duan, *Large-area graphene-nanomesh/carbon-nanotube hybrid membranes for ionic and molecular nanofiltration,* **Science 364**(6445), 1057 (2019). doi: 10.1126/science.aau5321
Impact Factor 2018: **40.443**	M.K. Masud, J. Na, M. Younus, M.S.A. Hossain, Y. Bando, M.J.A. Shiddiky, Y. Yamauchi, *Superparamagnetic nanoarchitectures for disease-specific biomarker detection*, **Chemical Society Reviews 48**(24), 5717 (2019). doi: 10.1039/c9cs00174c
Impact Factor 2018: **38.887**	Q. Jin, S. Jiang, Y. Zhao, D. Wang, J.H. Qiu, D.M. Tang, J. Tan, D.M. Sun, P.X. Hou, X.Q. Chen, K.P. Tai, N. Gao, C. Liu, H.M. Cheng, X. Jiang, *Flexible layer-structured Bi_2Te_3 thermoelectric on a carbon nanotube scaffold*, **Nature Materials 18**(1), 62 (2019). doi: 10.1038/s41563-018-0217-z
Impact Factor 2018: **38.887**	Y.Q. Li, M. Buerkle, G.F. Li, A. Rostamian, H. Wang, Z.X. Wang, D.R. Bowler, T. Miyazaki, L.M. Xiang, Y.Asai, G. Zhou, N.J. Tao, *Gate controlling of quantum interference and direct observation of anti-resonances in single molecule charge transport*, **Nature Materials 18**(4), 357 (2019). doi: 10.1038/s41563-018-0280-5

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J.K. Gimzewski


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F.M. Winnik

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J. Nara
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R. Tamura
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Emergent Materials Property Theory Group


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Y. Nonomura
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First Principles Simulation Group


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K. Kobayashi
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Principal Engineer

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J. Labuta


M. Matsumoto


L.W. Sang


M. Tenjimbayashi


D. Umeyama

Nano-Systems


G. Imamura


T. Konoike

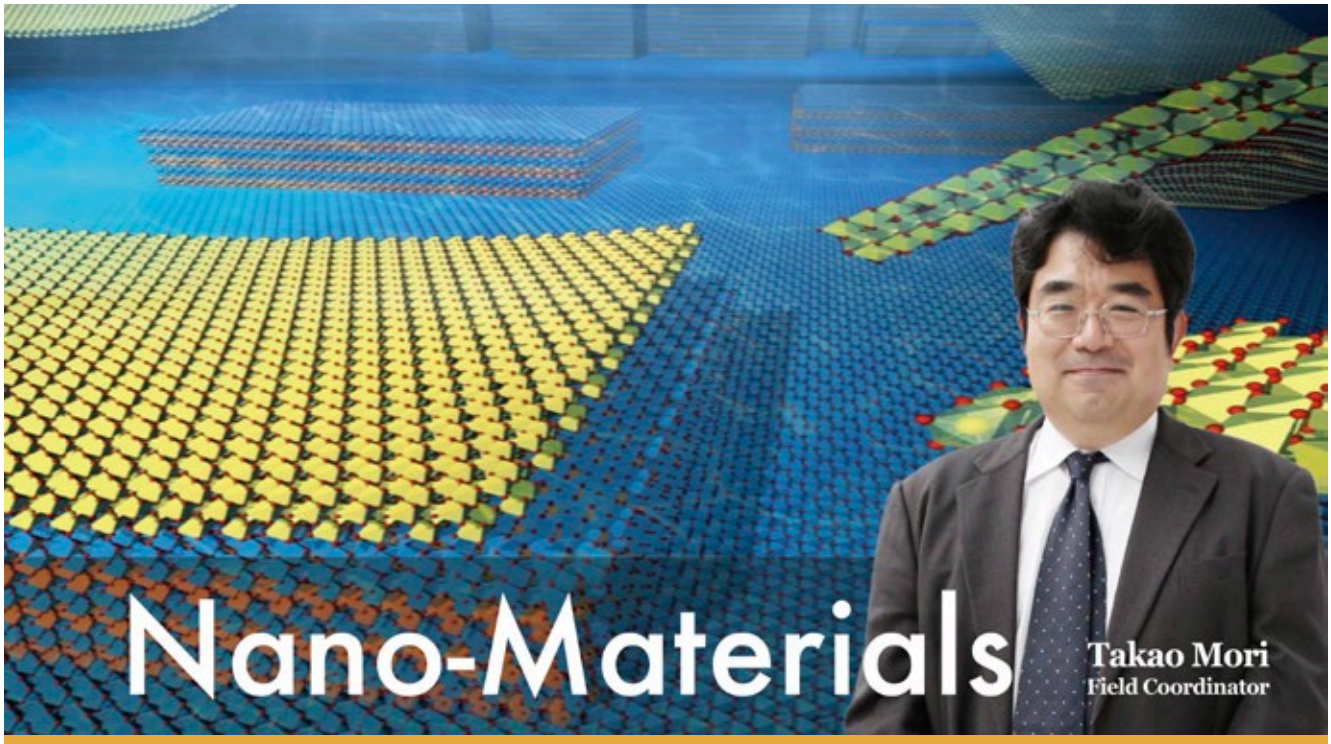

A. Okamoto


K. Uto

ICYS WPI-MANA Researcher (1):

Nano-Materials


T. Iwasaki



10 Research Groups

- Thermal Energy Materials Group
- Soft Chemistry Group
- Supermolecules Group
- Nanostructured Semiconducting Materials Group
- Nanotubes Group
- Mesoscale Materials Chemistry Group
- Photocatalytic Materials Group
- Functional Nanomaterials Group
- Nano Electronics Device Materials Group
- Frontier Molecules Group

Creating new materials and eliciting novel functions by sophisticated control of compositions and structures at the nano level

Making full use of MANA's advanced chemical synthesis technologies, beginning with soft chemistry, supermolecular chemistry and template synthesis, we are researching the creation of new nanomaterials such as nanotubes, nanowires, and nanosheets. Based on a wide range of material systems, spanning both organic and inorganic materials, we aim to discover novel physical properties and phenomena arising from size and shape in the nanometer range. MANA also develops and owns cutting-edge characterization facilities, including an integrated system of the transmission electron microscope with the scanning probe microscope, and is actively using these instruments for in-situ analysis of individual nanomaterials. In addition, we are promoting chemical nano- and mesoarchitectonics, in which these nanomaterials are precisely arranged, integrated and hybridized in the nano-to-meso range. By constructing artificial nanostructured materials in a designed manner, our aim is to create new materials that will exhibit advanced, innovative functions, and contribute to progress in a wide range of technological fields, including electronics, energy and the environment.

Thermal Energy Materials Group

Development of Thermal Energy Materials

Keywords: Thermoelectric Materials, Thermoelectric Power Factor

Group Leader
Takao MORI
(Field Coordinator, Principal Investigator)

1. Outline of Research

Approximately two thirds of primary energy (fossil fuels, etc.) being consumed in the world, sadly turns out to be unutilized, with much of the waste being heat. It is imperative to develop better thermal management (insulators, thermal dissipation, etc.) materials. Direct conversion of heat to electricity is also a large incentive to find viable thermoelectric (TE) materials, and we are developing novel materials and enhancement principles.

2. Current Topics

(1) Novel concepts for TE enhancement. We have discovered and demonstrated utilizing magnetism to enhance TE properties, namely, definitely showing that magnetic interaction and spin fluctuations,[1] respectively, can enhance the Seebeck effect, in the prototypical TE Bi_2Te_3 and Heusler alloy Fe_2VAl, respectively. Compared to magnon drag, spin Seebeck, etc. which are dependent on the magnetic ordering and/or application of magnetic fields, and thereby bound by low temperatures or low performance, the enhancement principles we have discovered are more robust and effective at relatively high temperatures, and also readily and widely applied. Excellent p, n control was obtained in the magnetic selenide Cr_2Se_3. As another principle of wide application, through doping we have manipulated the crystal field and obtained an enhancement of ZT~1.6 in GeTe.

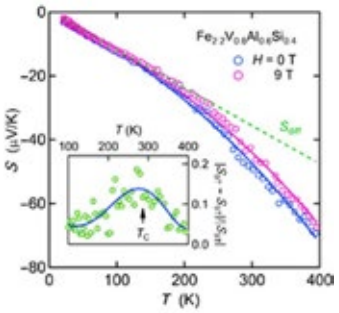


Fig. 1. Spin fluctuation enhancement of Seebeck coeff. in a Heusler alloy.[1]

(2) Nanostructuring to enhance TE. We have previously shown effects of nanopores to enhance ZT in rare earth-free skutterudite by phonon selective scattering. Through excess Te doping, much of which was evaporated to create pores, we achieved a 100% enhancement in ZT of the CoSbS sulfide. Fabrication of thin films is another powerful method to enhance the TE properties and several striking results were obtained in collaboration.[2]

References

1) N. Tsujii, A. Nishide, J. Hayakawa, T. Mori, *Sci. Adv.* **5**, eaat5935 (2019).
2) B. Hinterleitner, I. Knapp, M. Poneder, Y. Shi, H. Müller, G. Eguchi, C. Eisenmenger-Sittner, M. Stöger-Pollach, Y. Kakefuda, N. Kawamoto, Q. Guo, T. Baba, T. Mori, S. Ullah, X.Q. Chen, E. Bauer, *Nature* **576**, 85 (2019).

Soft Chemistry Group

Inorganic Nanosheets

Keywords: Nanoscale assembly of nanosheets, Functional nanosheets

Group Leader
Takayoshi SASAKI
(MANA Director, Principal Investigator)

1. Outline of Research

We aim at synthesizing 2D inorganic nanosheets as a unique class of nanoscale materials by delaminating various layered compounds through soft-chemical processes. These colloidal nanosheets are organized as a building block into various nano- to mesoarchitectures. On the basis of this approach, we design new and advanced functionalities.

2. Current Topics

We assembled colloidal 2D materials such as 1T MoS_2, Fe-Ni layered double hydroxide (LDH) and reduced graphene oxide (rGO) via electrostatic interaction into three types of heteroassembled composites.[1] Various characterizations including TEM (Fig. 1a), XRD and EDX support for the formation of a superlattice-like structure where two different nanosheets are alternately stacked at a molecular level. We examined electrocatalytic performance for OER and HER activities of the fabricated samples and found the heteroassembled superlattice composites showed the performance superior to those for restacked samples composed of single nanosheets (Fig. 1b). Particularly, the superlattice composite of MoS_2/LDH showed high activities for OER and HER with notably small overpotential values, enabling efficient overall water splitting. We fabricated

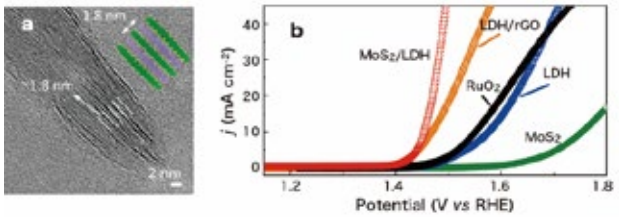


Fig. 1. (a) TEM image of MoS_2 / Ni-Fe LDH superlattice composite. (b) OER linear sweeping voltammetry curves of LDH and MoS_2 nanosheets, LDH/rGO and MoS_2/LDH superlattices and commercial RuO_2 in 1M KOH solution.

a two-layer stack of $Ti_{0.87}O_2$ nanosheets and rGO via the solution process.[2] The former nanosheets were deposited on a Si substrate via Langmuir-Blodgett process followed by drying a diluted suspension of rGO. Then, the electron beam lithography was applied to fabricate microelectrodes on the two-sheet stack. We found that upon exposure to UV light, excited electrons generated in $Ti_{0.87}O_2$ nanosheets were transferred to rGO to show efficient photocharge accumulation.

References

1) P. Xiong, X. Zhang, H. Wan, S. Wang, Y. Zhao, J. Zhang, D. Zhou, W. Gao, R. Ma, T. Sasaki, G. Wang, *Nano Lett.* **19**, 4518 (2019).
2) X. Cai, L. Yin, N. Sakai, D. Liu, C. Teng, Y. Ebina, R. Ma, T. Sasaki, *ACS Appl. Nano Mater.* **2**, 6378 (2019).

Supermolecules Group

Supramolecular Materials

Keywords: Molecular machines, Carbon materials, Interfaces, Self-assembly, Supramolecular concept

Group Leader
Katsuhiko ARIGA
(Principal Investigator)

1. Outline of Research

Functional materials have been carefully constructed using bottom-up approaches as can be seen in preparation of molecular and nano patterns, complexes, and nanomaterials with organized nano- and microstructures, and functional materials. We are working in exploratory research for innovative materials and sensing systems based on supramolecular concepts from the single molecule level to living cell dimensions.[1-5]

2. Current Topics

Multimodal switching of a redox-active macrocycle has been successfully demonstrated (Fig. 1).[1] Intramolecular charge-transfer states, involving hemiquinhydrones are probed and these interactions are used to construct an oxidation-state-coupled molecular switching manifold that reports its switch-state conformation through striking variation in its electronic absorption spectra. This molecular switching manifold exploits intramolecular coupling of multiple redox active substituents within a single molecule. These materials have potential for use in molecular logic or sensing applications.

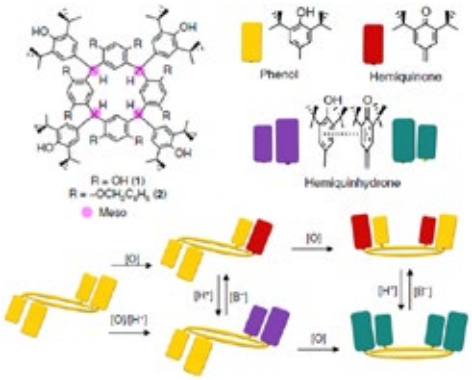


Fig. 1. Transformations involving oxidation of phenol groups (yellow blocks) to hemiquinonoid (red blocks), and quinhydrone activity of the resulting compounds denoted by purple for rctt-2-[Ox1] and turquoise for rccc-2-[Ox2]. [O] denotes oxidation; [H+] and [B−] denote acid and base, respectively.

References

1) D.T. Payne, W.A. Webre, Y. Matsushita, N.Y. Zhu, Z. Futera, J. Labuta, W. Jevasuwan, N. Fukata, J.S. Fossey, F. D'Souza, K. Ariga, W. Schmitt, J.P. Hill, *Nat. Commun.* **10**, 1007 (2019).
2) T. Mori, H. Chin, K. Kawashima, H.T. Ngo, N.J. Cho, W. Nakanishi, J.P. Hill, K. Ariga, *ACS Nano* **13**(2), 2410 (2019).
3) X. Jia et al, Adv. Mater., in press. DOI: 10.1002/adma.201905942.
4) G.J. Richardson, et al., *J. Am. Chem. Soc.*, in press. doi: 10.1021/jacs.9b10952
5) Q. Tang et al, ACS Nano, in press.

Supermolecules Group

Semiconductor Devices of Organic Nano-Sheet Crystals

Keywords: Organic Nano-sheet Crystals, Mechano-electronics

Principal Investigator
Junichi TAKEYA
(The University of Tokyo, Japan)
Cross Appointment with NIMS

1. Outline of Research

It is known that periodically arrayed two-dimensional sheets of molecules can generate diverse functions of cell-biology, regulating communication between inner outer circumstances. Self-assembling nature of the molecules, soft dynamics and large area-to-volume ratio are substantial in such functionalization. In our recent studies of elongated π-conjugated semiconducting molecules, we found that soft nano-sheet single crystal films are self-organized to the size of 10 cm x 10 cm and that the electronic device performance is maximized.

2. Current Topics

Self-organization of Organic Nano-sheet Crystals. Fig. 1 shows an example of the semiconducting molecules which grows to wafer-scale molecular layer crystals. The molecules of alkylated dinaphthobenzodithiophene (Cn-DNBDT) are first dissolved in organic solvents and are gradually crystallized during evaporation of the solvents at bottom surface of a blade in our home-made equipment with sliding substrate (Fig. 1). By properly adjusting temperature and speed of the crystal growth, it is found that a-few-monolayer crystal films are reproducibly grown to the size 10 cm x 10 cm.[1] We grew a bi-layer single-crystal

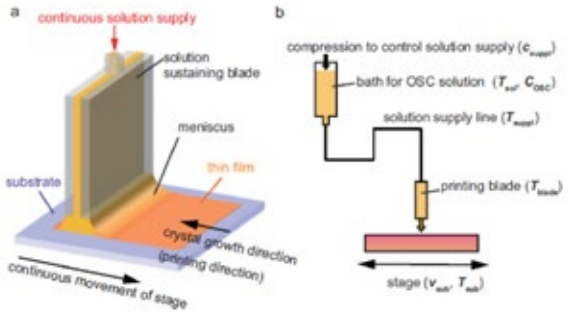


Fig. 1. Schematic image of the method of crystallization from solution.

film of Cn-DNBDT on a plastic substrate and field-effect transistors (FETs) are formed based on the nano-sheet crystal film. It turned out that the bi-layer film is highly homogeneous so that the mobility of nearly 1,000 FETs are distributed within 1% standard deviation. Integrated circuits of such organic single-crystal FETs are already fabricated to demonstrate such functions as tag identification and sensor operation.

Reference

1) S. Kumagai, A. Yamamura, T. Makita, J. Tsurumi, Y. Y. Lim, T. Wakimoto, N. Isahaya, H. Nozawa, K. Sato, M. Mitani, T. Okamoto, S. Watanabe, J. Takeya, *Sci. Rep.* **9**, 15897 (2019).

Nanostructured Semiconducting Materials Group

Next-Generation Semiconductor Nanodevices

Keywords: Nanowires, Semiconductor, GeSn

Group Leader
Naoki FUKATA
(Principal Investigator)

1. Outline of Research

Using one-dimensional nanowires, we are exploring high-mobility transistors, high-efficiency photoelectric conversion devices, and new device applications. Silicon (Si) and germanium (Ge) NWs have attracted particular attention due to their compatibility with current Si complementary metal-oxide semiconductor (Si CMOS) integrated circuit technology and their better scalability.

2. Current Topics

Germanium Tin ($Ge_{1-x}Sn_x$) alloy nanowires (NWs) with high Sn content have attracted great attention for their high carrier mobility, indirect-to-direct bandgap transition and Si-compatibility. However, the low equilibrium Sn concentration in Ge (<1 %) has to be overcome to realize high-speed MOSFETs or optical devices. To increase Sn content in $Ge_{1-x}Sn_x$ NWs and develop novel devices, the growth mechanism has to be understood. We investigated the effects of Sn concentration in catalysts along the growth direction, Sn incorporation into GeNWs and crystallinity of $Ge_{1-x}Sn_x$ NWs. The growth direction strongly depended on the Sn concentration in catalysts and the preferential orientation was changed from <111> to <110> by increasing the Sn concentration in the catalysts (Fig. 1).

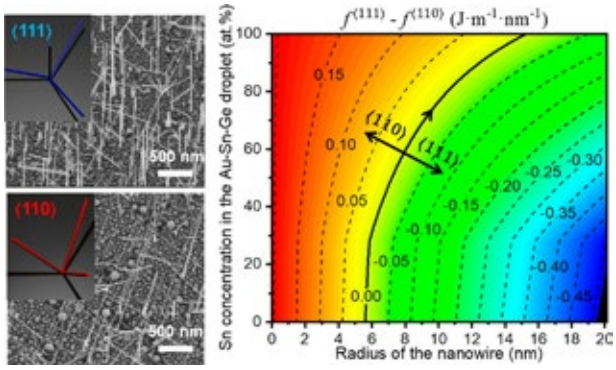


Fig. 1. SEM images of (a) ⟨111⟩- and (b) ⟨110⟩-oriented NWs grown on Si (111) substrate. (c) Contour plot of the separation between the free energy per unit circumference of the ⟨111⟩ and ⟨110⟩-oriented NWs as a function of NW radius and Sn concentration in a catalystaoplet.

High Sn content in Au-Sn catalysts also leads to high crystallinity of the $Ge_{1-x}Sn_x$ NWs. By applying a model proposed by Schmidt et al, we could successfully explain the results and elucidated that the main factor determining the growth direction of $Ge_{1-x}Sn_x$ NWs is the surface energy.[1)]

Reference

1) Y. Sun, R. Matsumura, W. Jevasuwan, N. Fukata, *Nano Lett.* **19**, 6270 (2019).

Nanotubes Group

Nanomaterial Properties Uncovered Under *in situ* TEM

Keywords: Nanotubes, Nanowires, Nanosheets

Group Leader
Dmitri GOLBERG
(Principal Investigator)
Cross Appointment with Queensland Univerisity of Technology, Australia

1. Outline of Research

Various properties of nanomaterials under full control of their morphology, crystallography, atomic structure, defect networks and spatially-resolved chemical compositions are studied using nanoscale manipulations and probing in a high-resolution transmission electron microscope (HRTEM) under ultimately high spatial resolution. Clear structure-property relationship is obtained which is a "Holy Grail" of Materials Science.

2. Current Topics

Intrinsic elastic modulus of multiwalled BNNTs and its dependence on created irradiation-induced defects have been studied via electric-field-induced high order resonance technique inside a high-resolution transmission electron microscope (HRTEM), Fig. 1. Resonance modes, up to 4th order, have been initiated in the cantilivered tubes and their moduli have been measured to be in a range of ~789 GPa to ~1003 GPa, with the standard deviation of 8.9 %, reducing the pre-existing in the literature BNNT moduli uncertainty by 54.6 %. Furthermore, electron irradiation in HRTEM has been used to mimic the cosmic rays radiation and to study the effects of defects onto elastic moduli. With an increase in the irradiation doze, the outer nanotube diameter has linearly reduced due to the knock-on effects.

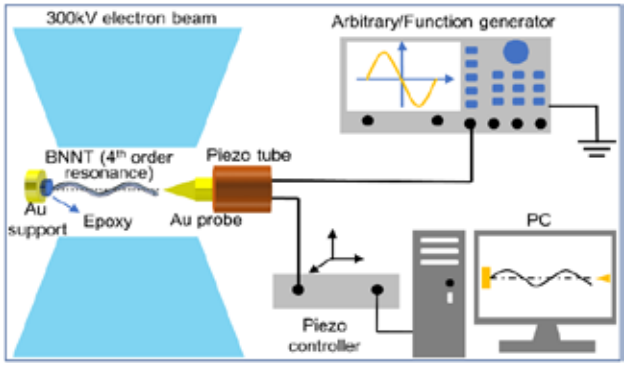


Fig. 1. Experimental setup for performing high-order resonance measurements of elastic modulus of individual multishell BN nanotubes.

Under irradiation a defective layer with nearly constant thickness has formed within the outer shells, and, as a result, the elastic modulus gradually decreases, albeit not dramatically, to ~663 GPa – still a very high value. Excellent intrinsic elastic properties and decent radiation-resistance prove that BNNTs could be a material of choice for applications in space.[1)]

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Mesoscale Materials Chemistry Group

Porous Graphene Nanomesh

Keywords: Mesoporous carbon, Nanosheets, Graphene

Group Leader
Yusuke YAMAUCHI
(Principal Investigator)
Cross Appointment with The University of Queensland, Australia

1. Outline of Research

Among series of two-dimensional (2D) materials, the widely identification of graphene nanomesh (GM), *i.e.*, porous graphene, is a relatively new concept of two-dimensional single- or few-layer of carbon nanosheet with in plane nanopores. In contrast to perfect graphene nanosheets which are prone to aggregate, GM have increased specific surface areas and accessible vertical pathway between the layers, which expand the application of GM in energy related systems. For example, the numerous nanoholes endow GMs with lots of defective edges, which probably provide extra active sites for catalyzing oxygen reduction reaction (ORR).

2. Current Topics

Here, we elaborately design a simple two-step dimensional reduction strategy for exploring nitrogen-doped graphene nanomesh by thermal exfoliation of crystal- and shape-modified metal–organic frameworks (MOFs).[1] MOF nanoleaves with 2D rather than 3D crystal structure is used as the precursor, which are further thermally unraveled into nitrogen-doped graphene nanomesh by using metal chlorides as the exfoliators and etching agent. Surprisingly, the prepared nitrogen-doped graphene nanomesh shows a unique ultrathin two-dimensional morphology, high porosity, rich and accessible nitrogen-doped active sites, and defective graphene edges, contributing to an unprecedented catalytic activity for oxygen reduction reaction in acid electrolytes (Fig. 1). This approach is suitable for scalable production and is probably universal for synthesis of thousands of novel low-dimensional functional carbon materials by breaking the dimensional limitation of traditional three-dimensional MOFs and further executing thermal exfoliation.

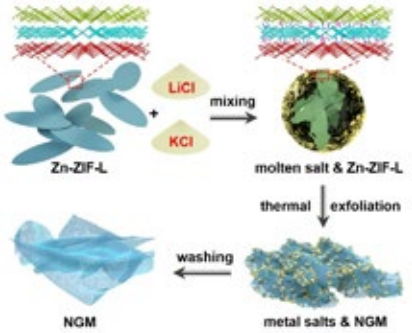

Fig. 1. Schematic illustration of the preparation process for GMs.

Reference

1) W. Xia, J. Tang, J.J. Li, S.H. Zhang, K.C.W. Wu, J.P. He, Y. Yamauchi, *Angew Chem Int Ed.* **58**, 13354 (2019).

Photocatalytic Materials Group

Hybrid Artificial Photosynthetic System

Keywords: CO_2 reduction reaction, Active sites, Reaction pathway, Selectivity

Group Leader
Jinhua YE
(Principal Investigator)

1. Outline of Research

We are conducting research and development of novel photocatalytic materials for a more efficient utilization of solar energy, as well as application of these materials for degradation of hazardous organics, solar hydrogen production and CO_2 conversion to useful hydrocarbon fuels. Our research approaches mainly include composition- and morphology-controlled fabrication of nanometals, organic/inorganic semiconductor materials and integration of those materials for advanced utilization of sunlight and efficient conversion to chemical energy.

2. Current Topics

Photocatalytic CO_2 reduction reaction (CO_2RR) toward chemical feedstocks relying on sunlight and suitable catalysts stands out as an attractive approach to CO_2 sequestration. The first and also critical step of the CO_2RR is how to activate the inert CO_2 molecules. Vacancies have been demonstrated to be significant for CO_2 reduction reaction (CO_2RR) over various oxide semiconductors, but anion vacancies were easily refilled with oxygen species and could work as both H_2 and CO evolution sites, aggravating the competition between hydrogen evolution reaction (HER) and CO_2RR. In this study, cation vacancies (V_{Zn}) were proposed as new active sites on the ZnS surface (Fig. 1). With no cocatalyst, the V_{Zn}-rich ZnS acquired a high selectivity of formate production (>85%) in inorganic aqueous solution. In situ attenuated total reflection-infrared (ATR-IR) spectroscopy and first-principle calculations have clarified the CO_2RR pathways into formate and proved that the surface V_{Zn} could greatly lower the barrier of CO_2RR and suppress the proton adsorption, elucidating the origin of the highly selective CO_2RR in the presence of competitive HER. This work gives an in-depth understanding of the cation vacancies and inspiration to develop efficient photocatalysts.[1]

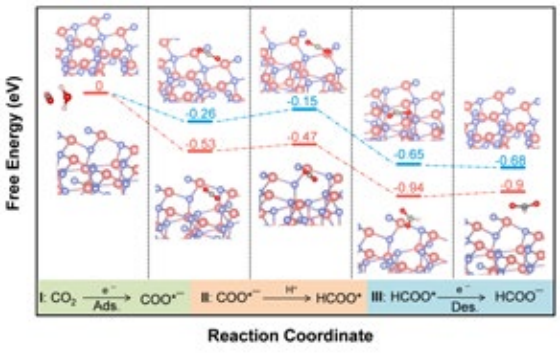

Fig. 1. Free energy diagram for the pathways of CO_2 conversion into formate on a perfect ZnS and VZn-ZnS surface.

Reference

1) H. Pang, X. Meng, P. Li, K. Chang, W. Zhou, X. Wang, X. Zhang, W. Jevasuwan, N. Fukata, D. Wang, J. Ye, *ACS Energy Lett.* **4**, 1387 (2019).

Functional Nanomaterials Group

Multifunctional Nanomaterials

Group Leader
Renzhi MA

Keywords: Single-layer nanosheets, Nano energy

1. Outline of Research

We work on the design and synthesis of different kinds of functional nanomaterials, particularly focusing on single-layer nanosheets. Various layered compounds including metal oxides, hydroxides and dichalcogenides, as well as graphite oxide are exfoliated under suitable conditions, yielding molecularly thin nanosheets. Ultimate 2D anisotropic feature and quantum effect of the nanosheets can radically increase accessible surface area, offer shortest ion diffusion and electron conducting paths, and thus induce emergent physicochemical properties. We are striving to explore diverse nanostructures and nanocomposites for energy-related applications.[1)]

2. Current Topics

We have demonstrated that the conductivity measured on single-layer nanosheets of layered double hydroxides (LDHs) was above 10^{-1} Scm^{-1} at moderate temperature and relative humidity (Fig. 1), the highest among reported ion conductors.[2)] We have further shown that, both experimentally and theoretically, hydroxide ions are derived from an efficient hydrolysis on basal planes, which proceed along 2D hydroxyl networks via a protonic-like Grotthuss mechanism. The superionic conduction was correlated with the hydroxyl network on nanosheet surface, which served as both free hydroxide ion donor and 2D hopping lane in the presence of water. In addition to

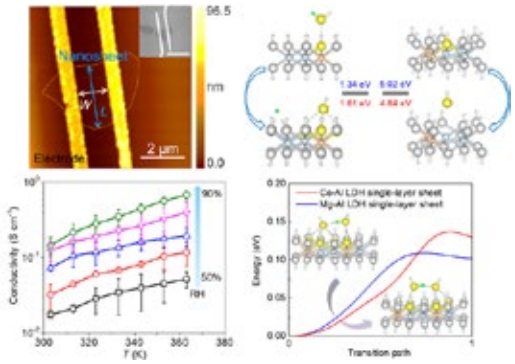

Fig. 1. Direct measurement and theoretic simulation of hydroxide ion conduction on single-layer LDH nanosheets.

providing new insights into superionic conducting behavior in nanostructures with ordered hydrogen-bonding surface/interface, the unique conduction mechanism unveiled in this study also reveals the great application prospects of 2D materials in constructing high-performance solid electrolytes/membranes for many renewable energy and bioelectronics applications.

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Nano Electronics Device Materials Group

Nano Electrics and Related Materials

Group Leader
Takahiro NAGATA

Keywords: Wide-band gap semiconductor, Gate insulator

1. Outline of Research

The development of high-dielectric constant film materials is essential for future active and passive nanoelectronics devices. For the development, we employ combinatorial synthesis, high throughput material development. In the nano electronics devices, there are many hetero interfaces, which influence the device performance directory. For the practical application, understanding the fundamental properties of the interface is also essential. Our group are developing the nano interface investigation technique for the nano electronics application also.

2. Current Topics

Silicon carbide (SiC) has recently attracted attention as a promising material for next-generation high-power high-frequency electronic devices. Recently, we developed a new spectroscopic method to observe the energy distribution of interface states based on operando hard x-ray photoelectron spectroscopy (OP-HAXPES). That is, photoelectron spectroscopic measurements are conducted under a bias voltage application between a metal layer and a semiconductor substrate. By applying OP-HAXPES on the SiO_2/4H-SiC(0001), we observed the energy distribution at the interface.[1)] The interface states have two components: a uniform structure spanning the SiC bandgap and sharp and large

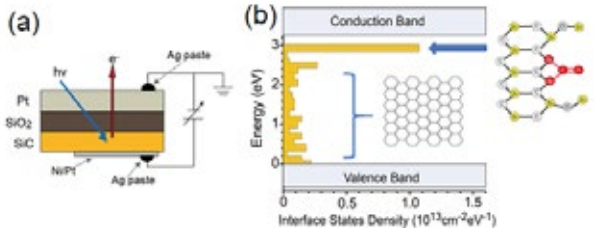

Fig. 1. (a) Schematic illustration of measurement setup. (b) Energy distribution of the interface states at SiO_2/4H- SiC(0001) interface and proposed models.

interface states near the conduction band minimum (Fig. 1). The uniform interface states are assigned to the carbon clusters, while the sharp interface states are attributed to the Si_2−C=O and/or Si_2−C=C−Si_2 states at the interface. We also revealed the relationship between band offset, gate leakage current, and interface states density at SiO_2/4H-SiC (000-1) interface by HAXPES.[2)] Our new measurement technique should contribute to the connection between the fundamental understanding and practical electronics device applications.

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Frontier Molecules Group

Functional Soft Molecular Materials

Group Leader
Takashi NAKANISHI

Keywords: Functional molecular liquids, Mechanical luminescent control, Liquid-electret

1. Outline of Research

We are working on synthesis of unique and frontier molecules/polymers possessing advanced functions and uncommon phenomena towards applications in sensor, actuator and so forth. Our research contains original molecular design, synthesis, self-assembly, molecular recognition and hybridization with other nanomaterials.

2. Current Topics

Newly developing functional soft matter/materials, namely "functional molecular liquids (FMLs)", are recently focused much attention toward the most promising candidate to be fabricated into stretchable (opto)electronic devices. In particular, solvent-free alkylated-π liquids exhibit excellent deformability, photo-/thermal- stability and predictable π-unit based optoelectronic functions. Here we introduce our recent developments (i) liquid electret,[1] and (ii) viscoelastic conjugated polymers.[2]

(i) Newly designed solvent-free liquid porphyrins show mechanoelectrical and electroacoustic functions as well as their stretchable performance (Fig. 1).[1] Our strategy of shielding π-unit of tetraphenylporphyrins with insulating flexible and bulky-alkyl chains are suitable for stably holding electric charges by the π-unit of liquid-porphyrins.

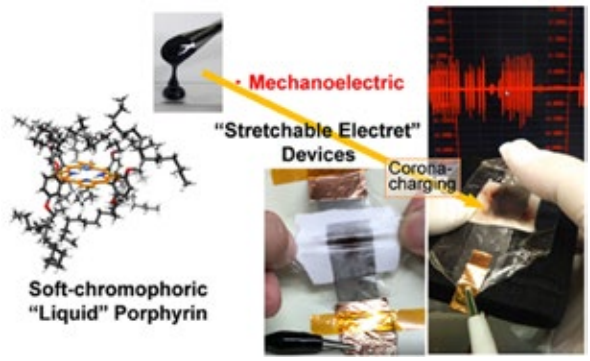

Fig. 1. Schematic structural model of a liquid porphyrin, and stretchable-mechanoelectric "liquid electret" device.

(ii) The solvent-free alkylated-π molecular liquid's strategy has been also extended to a conjugated polymer system. The creation of viscoelastic conjugated polymer (VE-CP) at room temperature, by using an intact π-conjugated backbone and flexible yet bulky-alkyl chains as internal plasticizers.[2]

References

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2) A. Shinohara, C.J. Pan, Z.F. Guo, L.Y. Zhou, Z.H. Liu, L. Du, Z.C. Yan, F.J. Stadler, L. Wang, *Angew. Chem. Int. Ed.* **58**, 9581 (2019).

MANA Satellite

Nanoscale Multimaterials with Complex Anisotropies

Principal Investigator
Gero DECHER
(MANA Satellite at University of Strasbourg, CNRS, France)

Keywords: Layer-by-Layer assembly method, Grazing incidence spraying

1. Outline of Research

Our team has a longstanding research interest in the assembly of nanoorganized multimaterials. Whereas the number of components in most of the present nano-composites is in the low single digit region, we have in the past developed the so-called Layer-by-Layer (LbL) assembly method[1] which has the largest choice of deployable components (inorganic salts, organic molecules, polymers, DNA, nanoparticles or biological objects including cells) among all existing techniques for surface functionalization.

2. Current Topics

LbL assembly allows to design and prepare nano¬scale materials composed of hundreds of different components with adjustable multifunctionality, a task close to impossible for most other self-assembly methods. Most of the current materials are isotropic, materials with anisotropic properties are in general more difficult to prepare and more difficult to characterize. Our team has introduced grazing incidence spraying[2] for aligning nano-wires, nano-rods and nano-fibers in-plane during the deposition of individual layers when building up LbL-assemblies (Fig. 1). With unidirectionally oriented multi¬layers one can for example fabricate multilayer films containing ultrathin polarizers. Grazing incidence spraying is, however, capable of producing more complex anisotropies even over large surface areas

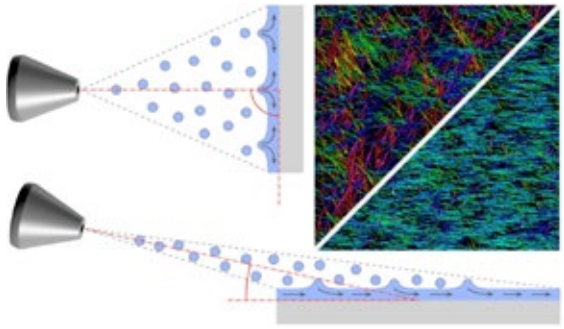

Fig. 1. Schematic depicting classic spray assisted LbL assembly which leads to isotropic films (top left) and grazing incidence spraying which produces films with in-plane anisotropy over large surface areas (bottom right).

by changing the direction of alignment in each individual layer of a multilayer film. The partnership between MANA and the University of Strasbourg allows us to continue to explore the assembly and properties of multifunctional multimaterial films and to compare nanocomposites with isotropic and anisotropic superstructures.

References

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MANA Satellite

Topochemical Reactions of Layered Materials

Keywords: Intercalation, Exfoliation

Principal Investigator
Thomas E. MALLOUK
(MANA Satellite at the University of Pennsylvania, USA)

1. Outline of Research

The topochemical reactions of layered materials are important in applications that include battery electrodes, supercapacitors, catalyst supports, high-k dielectrics, lubricants, and composites. Although much progress has been made in understanding their intercalation, exfoliation, and restacking reactions, quantitative measurements of the thermochemistry of these processes has been lacking. We have used isothermal titration calorimetry (ITC) to obtain quantitative data on the driving forces of these reactions.

2. Current Topics

Our laboratory has developed a suite of mild chemical reactions for the intercalation, exfoliation, and functionalization of layered metal oxides, transition metal dichalcogenides, boron nitride, and graphene.[1] One of the most interesting discoveries in this research is the strong bonding interaction between late transition metal ions and early transition metal oxide nanosheets, which arises from d-orbital acid-base interactions. We have used ITC to correlate the strength of these interactions with the stabilization of small clusters and individual atoms on the oxide nanosheet surface.[2] More recently, we have used ITC to measure enthalpy and entropy changes associated with the individual steps of intercalation, exfoliation, and restacking of the lamellar Dion-Jacobson phase perovskite $Na_{0.24}H_{0.76}Ca_2Nb_3O_{10}$. By measuring these values around a thermochemical cycle it is possible to calculate the enthalpy and entropy changes for transforming a three-dimensionally ordered layered solid into a turbostratically ordered re-stacked compound of the same composition (Fig. 1). Measurements of the individual steps in this cycle provide new insight into their driving forces, showing for example that the reaction of NaOH with $HCa_2Nb_3O_{10}$ is largely enthalpy-driven, whereas there is a strong entropic driving force for re-stacking of the exfoliated nanosheets by addition of sodium salts.

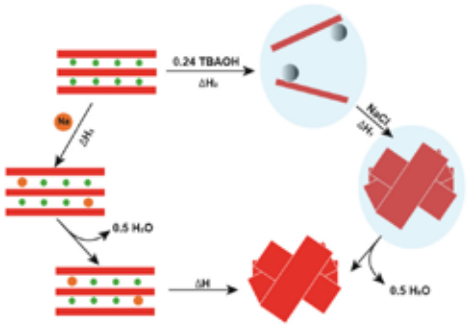

Fig. 1. Thermochemical cycle of the exfoliation/restacking reactions for the layered niobate, $HCa_2Nb_3O_{10}$. ΔH_1, ΔH_2, and ΔH_3 represent heats of reaction of (1) $TBA_{0.24}H_{0.76}Ca_2Nb_3O_{10}$ with NaCl, (2) $HCa_2Nb_3O_{10}$ with TBA^+OH^-, and (3) $HCa_2Nb_3O_{10}$ with Na^+OH^-.

References

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MANA Satellite

2D Piezotronics in Atomically Thin Zinc Oxide Sheets

Keywords: Piezotronic effect, Interfacing gating effect, ZnO nanosheet

Principal Investigator
Zhong Lin WANG
(MANA Satellite at Georgia Tech, USA)

1. Outline of Research

Using the inner crystal out-of-plane potential generated by the piezoelectric polarization charges created at atomically thin ZnO surfaces under stress/strain to simultaneously modulate the metal-ZnO Schottky barrier height and the conductive channel width of ZnO, the electronic transport processes in the two-terminal devices are effectively tuned by external mechanical stimuli. As decreasing the thickness of ZnO from tens of nanometre to atomic scale, the gauge factor is improved to ~2×10^8. The strain sensitivity is enhanced by over three orders of magnitude.[1]

2. Current Topics

The two terminal devices fabricated with metal-semiconductor-metal (M-S-M) structure are packaged by polymethyl methacrylate (PMMA) (Fig. 1a). In this configuration, the stress-induced opposite piezoelectric polarization charges present at the entire surfaces of the ZnO nanosheet, which will have a huge influence on the concentration and distribution of free carriers in all regions of the 2D film due to its atomic thickness. For the 2D piezotronic device, the current increases steadily with the increase of compressive stress (Fig. 1c). The changes in the electrical transport arise from the joint modulation of two effects: the interfacing gating effect, in which stress-induced piezoelectric polarization charges at metal-ZnO interfaces modulate the Schottky barriers, and the Channel width gating effect, in which stress-induced piezoelectric polarization charges at the top and bottom surfaces of ZnO control theconductive channel width (Fig. 1b).

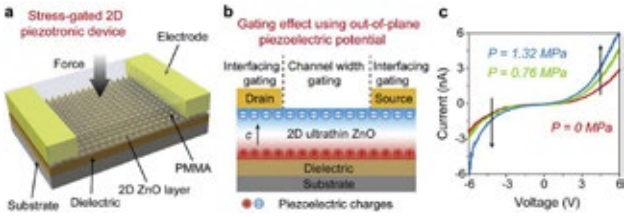

Fig. 1. Stress gated 2D ZnO piezotronic devices and the working mechanism. a,Schematic illustration of the 2D ZnO piezotronic device. b, Physical mechanism of the 2D piezotronics: Gating effect of stressinduced piezoelectric polarization charges at entire surfaces of atomically thin ZnO sheet. c, The modulation of carrier transport in the 2D piezotronic device under compressive stresses.

Reference

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Independent Scientist

Nanofiber Composite Monoliths for Thermal Insulation

Keywords: Macroporous monoliths, Thermal insulation

Independent Scientist
Gen Hayase

1. Outline of Research

Macroporous monolithic materials prepared by a sol-gel process, such as aerogels, have been studied for application to heat insulation. Due to the increasing interest in environmental problems in recent years, those low-bulk-density materials are expected to be used for energy saving. However, such materials are so fragile that their application is still limited. By compositing metal oxide nanofibers into a fine skeleton, we aim to produce high-performance insulation materials with practical strength.

2. Current Topics

Porous materials have been used as heat insulating materials since ancient times, and various materials such as glass wool and urethane foam are utilized today. As environmental problems increase, materials with superior thermal insulation are required to be developed. However, high-performance thermal insulation materials such as aerogels (thermal conductivity, $\lambda \sim 15$ mW m^{-1} K^{-1}) have a problem of poor mechanical strength due to their fine structure. We are researching to fabricate a high-strength composite structure by adding boehmite (AlOOH) nanofibers to a starting material (sol). The mechanism of the skeleton formation and the physical properties of the obtained monolithic materials have been investigated to develop another new process for obtaining composite structures with various compositions. These materials composed of silicone, silsesquioxane,[1] and phenolic resin (Fig. 1)[2] have excellent processability as well as mechanical strength. In addition to thermal insulation, we are developing surface applications not found in conventional macroporous materials.

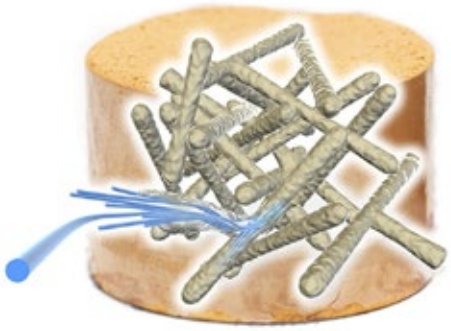

Fig. 1. Schematic image of a nanofiber composite monolith.

References

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Independent Scientist

Porphyrin Derivatives for Sensing Applications

Keywords: Porphyrin, Sensing, Chirality, Anions

Independent Scientist
Jan LABUTA

1. Outline of Research

Porphyrins are widely studied functional dyes. They have essential role in biological systems in the form of heme or photosynthetic antenna. In our research we focus on utilization of porphyrin (TPP) and oxoporphyrinogen (OxP) derivatives (Fig. 1) for sensing applications, such as enantiomeric excess sensing, colorimetric pH detection or determination of trace water impurities in organic solvents.

2. Current Topics

TPP can be used as a prochiral chiral solvating agent (pro-CSA) for NMR detection of enantiomeric excess (*ee*) of chiral organic acids.[1] The pro-CSA sensing mechanism is not based on formation of diastereomers. This is in contrast with standards NMR techniques. In the pro-CSA sensing mechanism the chiral information is translated from chiral analyte (acid) to porphyrin and manifests itself as chemical shift nonequivalence of the NMR signals of TPP's β-protons. We have investigated various factors affecting the sensing mechanism, such as temperature, guest exchange rate and binding strength. These findings yield insight for design of the next generation of *ee* sensing molecules. The OxP (a oxidized form of porphyrin) molecule exhibits interaction with common chloride and nitrate anions (in the form of salts).[2] Combined analysis of ^{1}H NMR and UV-vis titration data enabled an evaluation of binding strengths of anions with OxP in an elaborate binding model where the anion salt dissociation process was also incorporated. The anions could be classified as two types based on their interactions with OxP: Type A anions (Cl^-, NO_3^-, HSO_4^-) associate as 1:1 complexes through hydrogen bonding while interactions involving Type B anions ($CH_3CO_2^-$, F^-, $H_2PO_4^-$) are complicated by deprotonation of OxP and/or countercation association. OxP derivatives represent promising candidates for detection of biologically relevant anions in solution.

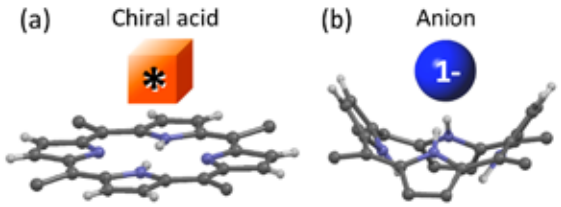

Fig. 1. Core structure of (a) flat tetraphenylporphyrin (TPP) and (b) saddle-shape oxoporphyrinogen (OxP).

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Independent Scientist

Synthesis of 2D Macromolecules and Their Use for Water Purification

Keywords: Semiconductor engineering, Power device application

Independent Scientist
Michio MATSUMOTO

1. Outline of Research

Recent massive developments in two-dimensional (2D) materials physics demand new methodologies to design and create new synthetic materials in this category. However, chemically synthesizing 2D macromolecules in atomic preciseness is still very challenging. We have targeted to answer these issues by studying covalent organic frameworks (COFs), and the new 2D COF materials obtained through our studies have been adapted to environmental technology applications.

2. Current Topics

2D COFs are an emerging class of porous and crystalline polymers prepared from small organic monomers. The structure, topology, and porosity of COFs are easily designed and controlled, based on simple geometric criteria of its monomers. The key of these COF syntheses is connecting monomers with dynamic covalent bonds and choosing reaction conditions that enhance their dynamicity. Thus imine-linked COF syntheses conventionally required high-temperature (70 °C), large-loading of acid-catalysts (acetic acids, 100 equiv.), and long reaction times (>72 h). We recently found $Sc(OTf)_3$, water-tolerant Lewis acid, can promote this COF reaction as an alternative catalyst

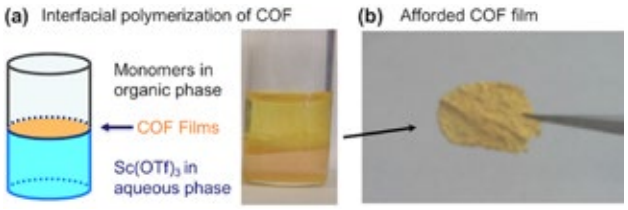

Fig. 1. (a) Schematic explanation and photo of interfacial polymerization of TAPB-PDA COF and (b) afforded COF free-standing film.

and significantly milden reaction requirements as room temperature and 10-minute reaction time even with a small loading amount (0.2 equiv.).[1] Furthermore, our new mild reaction conditions with $Sc(OTf)_3$ realized interfacial polymerization of COFs by introducing phase separation of reaction solvents, affording COF free-standing films (Fig. 1).[2] The obtained COF films are adapted to top layer of water purification membranes and exhibited rejection of small organic water pollutant surrogates from water.

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Independent Scientist

Semiconductor Interface Engineering for Power Device Application

Keywords: III-Nitrides, Interface engineering

Independent Scientist
Liwen SANG

1. Outline of Research

As one of the promising candidates for the high-frequency and high-power electronic devices, III-Nitride GaN has been leading the research and application in the RF communications. With the increasing power, the reliability becomes the biggest issue, and all the reliability problems are finally attributed to the interfaces. For example, the defects at the MIS interface induced the threshold voltage instability. The thermal boundary resistance leads to large-density heat concentration. Our research is to solve the reliability issues in the GaN electronic devices by using the interface engineering.

2. Current Topics

MOS interface defects control.[1] It was found that, the interfacial oxidized layer at the MOS structure is the main reason for the large-density traps. However, this layer can't be simply removed by the chemical treatment. To avoid re-oxidation, our strategy is to utilize the oxygen-free dielectric layer such as CaF_2, SiN_x for the p-GaN MISFETs. The interface state density and traps density were both drastically reduced. The mechanism was investigated from the understanding of the MIS microstructure. With the support of the originally developed two-step surface treatment, the trapped charge density was reduced by 2 orders of magnitude. The high-quality CaF_2/p-GaN

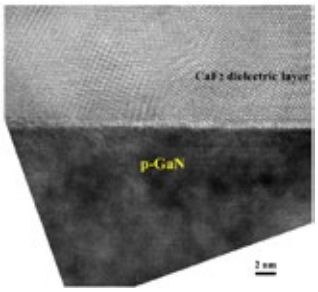

Fig. 1. Good interface at p-GaN/CaF_2 MIS structure.

interface is shown in Fig. 1.

Polarization engineering at nano-interface for the carriers/phonon transportation.[2] To improve the carrier transportation, we propose to deposit the compositional gradient multiple layer and engineer the 2D hole gas to 3D transportation. The highest hole mobility was achieved in the p-InGaN. The phonon transportation can also be engineered with the piezoelectric polarization field to enhance the thermal dissipation of the electronic devices.

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Independent Scientist

Wetting Dynamics for Liquid Repellent Surfaces

Keywords: Wetting, Soft matter interface

Independent Scientist
Mizuki TENJIMBAYASHI

1. Outline of Research

We study the structure and dynamics of interfaces based on fundamental physical laws. Major topic is wetting of soft materials. Wetting phenomena are ubiquitous in nature and technology. Thus, understanding the wetting dynamics lead to the unachieved design of biomimetic materials, wet processing, and functional interfaces. These outcomes are applied for solving energy and environmental issues, which is our final goal.

2. Current Topics

Our major topic is to understand "How to prevent unwanted adhesion to surfaces." Research targets are fingerprint, snow, mist, nucleated ice, fluidic food, polymer melt, biomaterials, and granular materials.[1] The outcomes will offer us ideas to design functional non-adhesion surface materials. We are now in the stage of understanding the dynamics of their adhesion processes by integrating high speed camera with custom-build optical set-ups.[2] One of our achievements is a design of super liquid-repellent coatings as shown in Fig. 1. The surface possesses both nano to micro scale hierarchical structure and hydrophobic surface chemistry. Water droplets rest on this surface exhibits water contact angle of ~170°, and they roll off this surface with small tilting of <5° without any adhesions. We expect this textile can be applied for non-fouling clothing industries, which leads to the significant decrease of laundry costs.

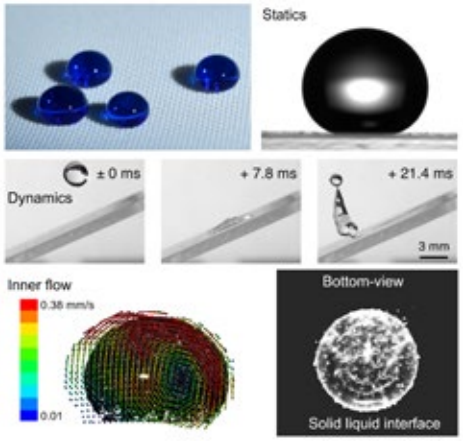

Fig. 1. A photo image of droplets rest on a super liquid-repellent textiles and various analysis tools for understanding wetting dynamics.

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Independent Scientist

Molecular Expansion of Layered Perovskites for Exotic Properties

Keywords: Controlling semiconductor bandgaps, Layered perovskites

Independent Scientist
Daiki UMEYAMA

1. Outline of Research

Means of controlling semiconductor bandgaps are of great importance in materials design. In particular, fabrication of layered heterostructures with controlled thickness and composition can be used to modulate the composites' electronic structures.[1] In my recent research, I have focused on lead-iodide hybrid perovskites, and investigated the optical properties of a self-assembled layered perovskite functionalized with thiocyanate ions.[2]

2. Current Topics

The three dimensional (3D) structure of lead-iodide hybrid perovskite (CH_3NH_3)[PbI_3] can be "sliced" with thiocyanate ions (SCN^-). By partially substituting the iodide ions with SCN ions, a two dimensional (2D) layered hybrid perovskite (CH_3NH_3)$_2$[$PbI_2(SCN)_2$] (sample **1**) is obtained (Fig. 1). I characterized the effect of the substitution in terms of optical and mechanical properties to rationalize structure-properties relationships. The ligand substitution to SCN ions reduces the dimensionality of the structure and enhances the effect of quantum confinement. This is clearly represented by the presence of exciton peak in the optical absorption spectrum of **1** even at room temperature.

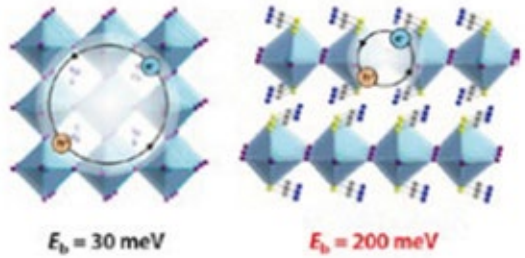

Fig. 1. Site-selective ligand substitution results in dimensional reduction of the lead-iodide perovskite.

On the basis of the absorption spectrum at 6 K, I determined the exciton binding energy as 200 meV (Fig. 1). The binding energy is higher than that of the 3D perovskite (CH_3NH_3)[PbI_3] (~30 meV) owing to quantum confinement in **1**; however, it is smaller than that of conventional 2D perovskite such as (CH_3NH_3)$_2$[$PbI_2(SCN)_2$] (~360 meV). This is most likely because the polarizable π electrons on SCN ions reduce dielectric confinement in **1**, providing a molecular strategy to controlling the excitonic behavior.

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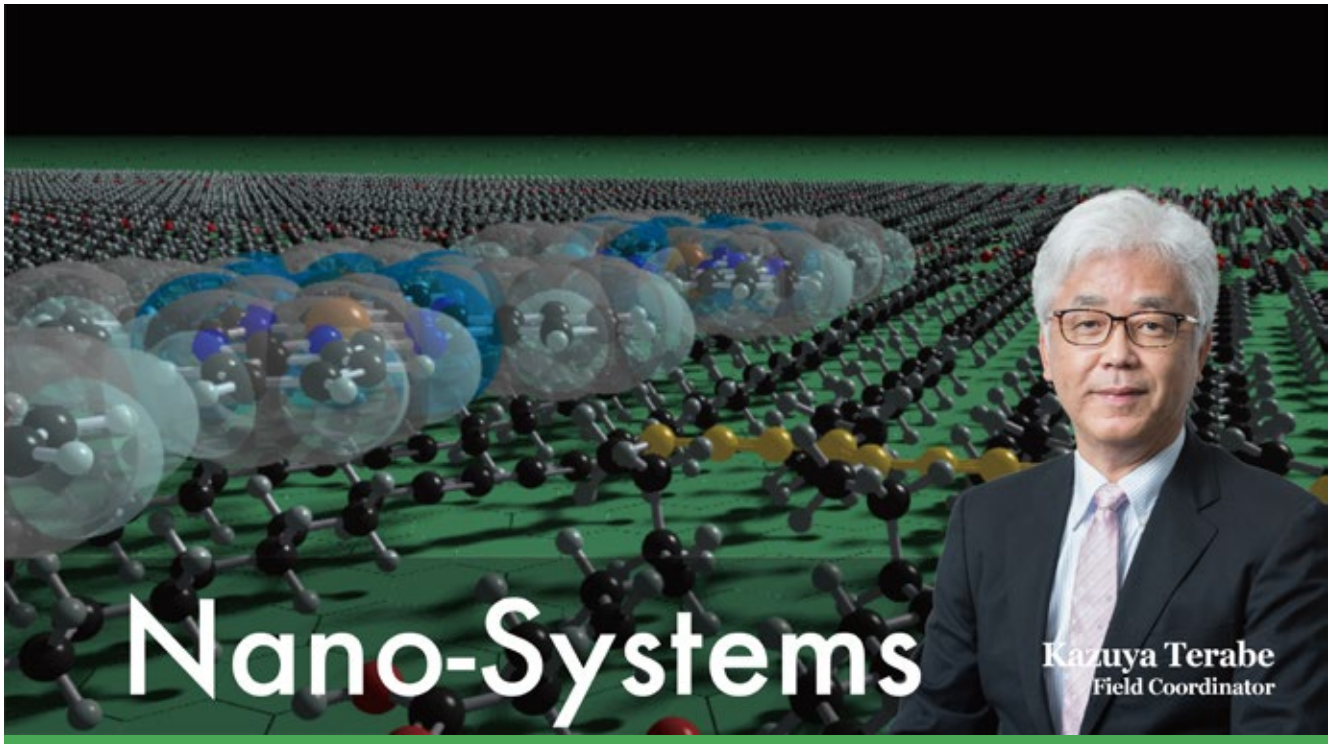

12 Research Groups

- Nanoionic Devices Group
- Nano Functionality Integration Group
- Quantum Device Engineering Group
- Nano-System Theoretical Physics Group
- Photonics Nano-Engineering Group
- Nano Frontier Superconducting Materials Group
- Thin Film Electronics Group
- Smart Polymer Group
- Medical Soft Matter Group
- Mechanobiology Group
- Surface Quantum Phase Materials Group
- Nanomechanical Sensing Group

New nano-systems are changing the world: from artificial intelligence to energy and the environment, diagnosis and medicine

This research field is searching for various nano-systems that will express novel functions by the interaction of nanostructures with unique characteristics, and is engaged in research to research to utilize those new nano-systems systematically. Concretely, based on basic research on nanoscale materials, such as atomic and molecular transport and chemical reaction processes, polarization and excitation of charge and spin and superconducting phenomena, we are conducting research on atomic switches, artificial synapses, molecular devices, new quantum bits, neural network-type network circuits, next-generation devices, high sensitivity integrated molecular sensors and other new applied technologies. Since the development of new nanoscale measurement methods is also a high priority, we are developing multi-probe scanning probe microscopes and other cutting-edge instruments. We also attach great importance to interdisciplinary fusion-type research with other research fields.

Nanoionic Devices Group

Atomically-Controlled Solid-State Electrolyte Films Toward Nanoionics

Keywords: Solid-state electrolyte thin film, Atomic layer deposition

Group Leader
Kazuya TERABE
(Field Coordinator,
Principal Investigator)

1. Outline of Research

Recently, much attention has been paid to fabricate solid-state electrolyte (SSE) films not only for solid-state battery applications but also for nanoionics applications such as memories, sensors, and neuromorphic computing. Several methods, such as sputtering and pulse-laser deposition, have been used to form SSE films, but they do not reach the controllability in composition and uniformity of deposition techniques for semiconductor materials. We are trying to fabricate SSE films in a layer-by-layer manner using atomic layer deposition (ALD).

2. Current Topics

We successfully fabricated a magnesium phosphate ($Mg_3(PO_4)_2$) film by developing a ternary ALD process consisting of Mg-O and P-O sub-cycles.[1] Very uniform amorphous films were obtained at relatively low temperatures ranging from 125 to 300 °C, as shown in Figs. 1a-1f. It was found that lower temperature deposition induces multi-bonding states in the phosphate matrix, which forms a mixture of pyrophosphates and metaphosphates. The film deposited at 125 °C exhibited higher ionic conductivity with a smaller activation energy than a sputtered magnesium phosphate film, as shown in Fig. 1g. The higher conductivity is attributed to enhanced hopping conduction of Mg ions in the disordered (multi-bonding) phosphate matrix. The results demonstrate the usefulness of ALD technique in realizing highly conductive Mg-based SSE films, which can be applicable for other SSE materials.

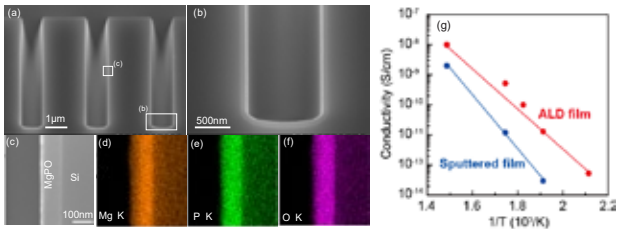

Fig. 1. (a) Cross-sectional SEM images of a 100 nm thick ALD magnesium phosphate film, deposited on a patterned trench structure. Magnified views at the bottom (b) and the sidewall (c) of the trench. The corresponding EDX mapping images for the Mg K edge (d), P K edge (e), and O K edge (f). (g) Arrhenius plot of the electrical conductivity for ALD and sputtered films, measured in the temperature range between 200 and 500 °C.

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Dr. Yuji Okawa (Chief Researcher) passed away on August 1st, 2019, at the age of 55.

Dr. Yuji Okawa moved from RIKEN to NIMS in 2002 with his five colleagues and became a key member of MANA from its founding in 2007. He opened new horizons in nanochemistry by demonstrating that a single electrically conductive polymer chain can be created at any designated positions in a certain film by initiating chain polymerization reactions using the probe tip of an STM. He had tried to further develop the method, while fighting with his illness. We are certain his dream will be realized by his younger successors.

Masakazu Aono
Founder & Executive Advisor of WPI-MANA
on behalf of all members of WPI-MANA

Nano Functionality Integration Group

Integration of Nano Functionality

Keywords: Multiple-probe scanning probe microscopes, Nanocarbon integration

Group Leader
Tomonobu NAKAYAMA
(MANA Deputy Director, Principal Investigator)

1. Outline of Research

We develop novel techniques and methodologies, based on scanning probe microscopy and related techniques. We aim to create nanomaterials and nanosystems that are realized by integration of appropriate nano parts. Multiple-probe scanning probe microscopes (MP-SPMs) are used to investigate electrical properties of nanomaterials and nanosystems.[1] Nanocarbon integration is studied with high-resolution atomic force microscopy (AFM).[2] A study on emergent dynamics of networks of unreliable elements[3] leads us to open a new research field of "synthetic intelligence."

2. Current Topics

Multiple-probe Scanning Probe Microscopes (MP-SPMs) control 2 to 4 scanning probes that are brought into electrical contact to a single nanostructure. Our latest MP-SPM is operated using a home-built control system and realizes flexible control over four independent probes. For example, Kelvin-probe force microscopy (KPFM) measurement under current flow in a single nanostructure is possible by placing two MP-SPM probes at designated sites of the structure to flow a current. The MP-SPM played a key role in developing neuromorphic nanowire networks which exhibit dynamical self-organization of conductive pathways through the networks. In such networks, a huge number of "synaptic" elements are interconnected randomly through metal nanowires and, as a result, brain-like functionalities have been found to emerge (Fig. 1).

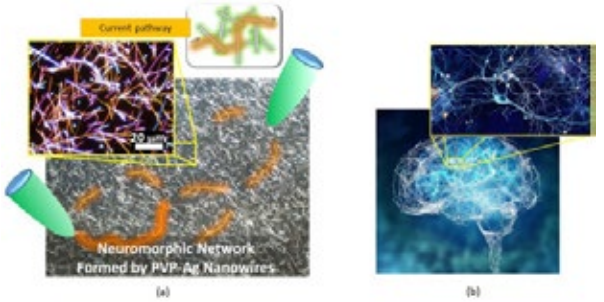

Fig. 1. (a) Micrograph of the neuromorphic network. The network contains of numerous junctions between nanowires which operate as synaptic elements. (b) A Human brain and a part of its neuronal network.

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Quantum Device Engineering Group

Electrolyte-Gated Organic Field-Effect Transistor for Cs Ion Sensing

Keywords: Organic FET, Ion sensor

Group Leader
Yutaka WAKAYAMA
(MANA Deputy Director)

1. Outline of Research

The radioactivity of Cs^+ ions produced in nuclear power stations (NPSs) causes serious impact on the health condition of humans, aquatic plants and animals. Therefore, it should be strictly controlled. However, a large amount of radioactive Cs^+ had been distributed from Fukushima NPS due to the tragic accident after the great earthquake in Japan. Because of these reasons, the detection and monitoring of Cs^+ ions in natural water are necessary. To tackle this issue, we developed an organic field-effect transistor (OFET)-based ion sensor.[1]

2. Current Topics

The sensor is composed of three main components: 1) organic semiconducting channel with high stability in natural water, 2) monolayer lipid membrane working as ultra-thin dielectric layer to allow low operating voltage and high sensitivity, and 3) novel calixarene-crown ether probe for high selectivity to Cs^+, which is grafted with lipid layer (Fig. 1). Once ion probes form metal-complex with Cs^+, the electrical signal from ions can be detected as a shift of threshold voltage, even the concentration of which is on the ppb order. This is owing to the large electrical capacitance of monolayer lipid membrane. In comparison with other conventional methods, our new sensor has many advantages: high sensitivity and selectivity, high-throughputs and portability for on-site monitoring. We developed a label-free sensor with the sensitivity of femtomolar (pg/l) concentrations of Cs^+ ion.

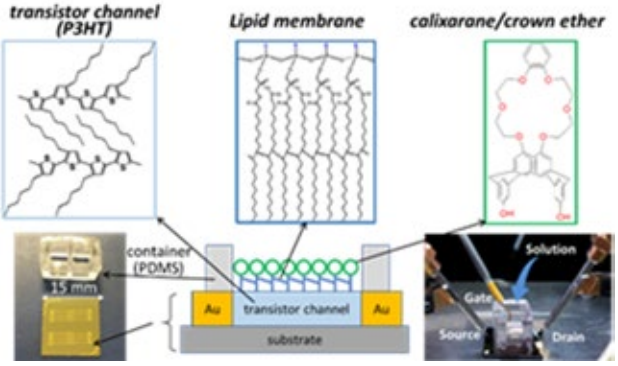

Fig. 1. Schematic illustrations and photographs of Cs ion sensor, transistor channel, lipid membrane and ion probe.

Reference

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Nano-System Theoretical Physics Group

High-Performance Topological Bulk Laser Based on Photonic Crystals

Keywords: Topological photonics, Topological nano laser

Group Leader
Xiao HU
(Principal Investigator)

1. Outline of Research

There has been a surge in searching for materials with topological features, whose transport properties are not influenced even the sample shapes are changed. Topological properties were first discovered in electron systems, and more recently the notion has been developed for electromagnetic waves, which is expected to be useful for building optic waveguides immune to backscattering and novel photonic functional devices.[1)]

2. Current Topics

This year we succeeded in developing a novel topological bulk laser.[2)] In our laser cavity, a bulk state of a topological photonic crystal around the band edge at Γ point is laterally confined by a trivial photonic crystal (Fig. 1) since they acquire opposite parities due to the band inversion. The band-inversion induced confinement occurs in a small range of wavevectors around the Γ point which provides a novel lasing-mode selection mechanism and renders emission directionality. These properties are distinct with topological lasers based on edge/interface states reported so far, and thereby we call the present device as topological bulk laser. The experimentally demonstrated topological bulk laser operates at room temperature in a single mode with a side-mode suppression ratio over 36 dB which remarkably reaches the requirement for most practical applications including telecommunication, laser printing and sensing according to IEEE and other industry standards. The threshold of the topological bulk laser is of the order of kW/cm^2 which as small as those found in commercial laser diodes. We show that the topological bulk laser emits vertically, despite its microscale cavity size.

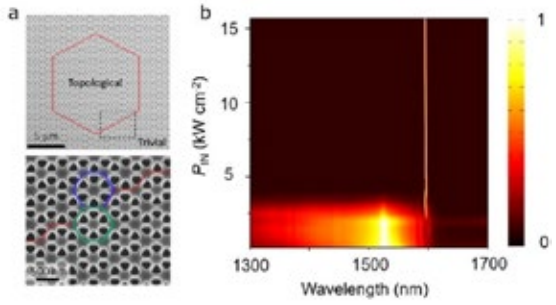

Fig. 1. Structure and power spectrum of topological bulk laser.

References

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Photonics Nano-Engineering Group

Materials and Devices for Nano-Scale Photo-Energy Transducers

Keywords: Infrared energy from sunlight, Photo-energy tranducers

Group Leader
Tadaaki NAGAO
(Principal Investigator)

1. Outline of Research

Most of the matters in universe emit thermal radiation and more than half of the solar radiation is composed of infrared light. So, harvesting infrared energy from sunlight as well as from thermal radiation associated with industry /human activity has become one of the important approaches towards the sustainable development goals (SDGs). Along with the device fabrications, we explore various types of plasmonic materials and nano-architectures with appropriate optical properties.[1,2)]

2. Current Topics

One of the important projects in our group is to realize high performance transducers that can convert thermal radiation to electricity.[2)] Such devices can be used as small-scale energy harvester as well as infrared color sensors for IoT products as well as in quality control in production lines. In the current study, we develop a spectroscopic infrared sensor with ultra-narrowband resolutions and high directivity in order to create a small-scale IR sensor capable of accurately seeing different materials and measuring the true temperature of objects without calibrating their emission intensity and temperature beforehand. The device shown in Fig. 1 showed the best IR performance - wavelength resolution as high as 50 nm with detection wavelength from 3 μm – 5 μm and directivity better then ±1°. Furthermore, we realized it in the form of multiband (*i.e.,* multicolour) IR sensors mounted on a single chip. This sensor can be used to create miniature IR spectrometers, remote true-temperature sensors, and a smart gas sensor capable of detecting many gas species in the air.

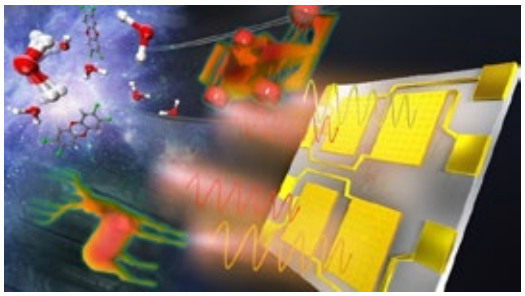

Fig. 1. An on-chip multi-wavelength IR sensor that can measure the thermal spectrum of matter.

References

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Nano Frontier Superconducting Materials Group

Tuning of the Physical Properties using Field-Effect Diamond Anvil Cell

Keywords: Field-effect, Electric double layer (EDL), Diamond anvil cell (DAC), High pressure

Group Leader
Yoshihiko TAKANO
(Principal Investigator)

1. Outline of Research

The application of high pressure enables us to reach unknown phenomena such as high-transition temperature superconductivity (HTS) where we could never have access at the ambient pressure. The recent discovery of HTS in hydrides using diamond anvil cell (DAC) is a typical example of research under high pressure. On the other hand, many interesting phenomena have been recently observed due to the introduction of carriers into materials, by using an electric double-layer transistor (EDLT) structure. When an EDL formed on a sample interface it induces a large number of carriers around the sample surface. The EDLT structure and the DAC are predominant tools for tuning of the physical properties in materials.

2. Current Topics

Our basic idea is to combine both EDLT and DAC to explore the new superconducting materials. We have designed new DAC with the micro-scale boron-doped diamond electrodes and the insulating un-doped diamond for the development of EDLT-DAC.[1)] We have discovered 10 new pressure-induced superconductors by using this DAC coupled with a data-driven approach.[1,2)] Based on this DAC, the ionic liquid for generating EDLT was used as a pressure transmitting medium. And then, we have found that Pt-Ir alloy has an electrochemically stable and enough hardness as a gasket. This new DAC device can realize EDLT structure in the DAC (Fig. 1(a-b)). We recently succeeded in the observation

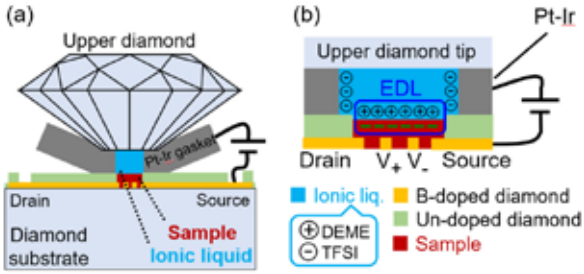

Fig. 1. (a) A schematic image of the EDLT-DAC and (b) the enlarged view around the sample space. The pressure medium is an ionic liquid (DEME-TFSI). The gasket (Pt-Ir alloy) also works as the gate electrode. The boron-doped diamond was used as the electrodes for measuring the resistance, and the un-doped diamond was used as the insulating layer.

of the field-effect in a film sample under high pressure using this EDLT-DAC. In the future study, our EDLT-DAC is expected to accelerate the exploration of new physical phenomena by tuning of the carrier density in the materials while applying high pressure.

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Thin Film Electronics Group

Organometallic Nanosheet for Organic Light-Emitting Devices

Keywords: Organometallic 2D nanosheet, Liquid/liquid interfacial process OLED

Group Leader
Kazuhito TSUKAGOSHI
(Principal Investigator)

1. Outline of Research

Atomically flat and dangling-bond-free surface of two-dimensional (2D) vdW materials not only provides an ideal interface for efficient carrier injection and transport but also enhance the resistance of 2D vdW materials to interact with other materials. The 2D vdW materials have been integrated into optoelectronic devices to achieve exceptional functionality. However, integration of large-area 2D thin film into organic light-emitting devices (OLEDs) remains challenging because finite number of inorganic 2D materials and high-temperature requirements of their deposition process. The construction of 2D organometallic materials holds an immense potential because of solution synthesis, unlimited structural and functional diversities.

2. Current Topics

We report a facile route using oil-water interfacial coordination reaction between organic ligand and divalent metal ion to synthesize crystalline quasi-2D organometallic bis(dithiolato)nickel (NiDT) nanosheet with centimeter scale and tunable thickness.[1)] The NiDT nanosheet can be directly integrated into OLEDs using as hole buffer layer and fluorescent mounting media without the aid of transfer process (Fig. 1). Moreover, OLEDs with NiDT nanosheet not only show comparable efficiency to conventional

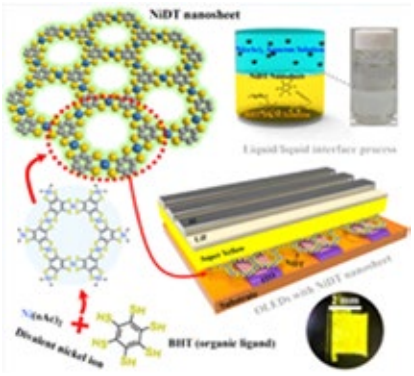

Fig. 1. We succeeded in synthesizing centimeter scale organometallic nanosheet and integrating the novel nanosheet into OLEDs as functional layer.

OLEDs, but also prolong their device lifetime to nearly two times. These results open up a new dimension to use quasi-2D organometallic nanosheets as functional layer in large-area organic devices. Collaboration with Prof. Nishihara (U. Tokyo) and T. Yasuda (NIMS).

Reference

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Smart Polymer Group

Smart Nanofibers for Cancer Therapy

Group Leader
Mitsuhiro EBARA

Keywords: Smart polymers, Nanofibers

1. Outline of Research

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

2. Current Topics

We have developed a smart anti-cancer fiber mesh that is able to control tumor-killing activity against lung adenocarcinoma precisely.[1] The proposed fiber system might provide a blueprint to guide the design of the next generation of local drug delivery systems for safe and effective cancer treatment. Effective cancer therapy can be achieved by designing a smart nanofiber system with the combination of chemotherapy and hyperthermia.[2] The mesh is composed of biodegradable poly(ε-caprolactone) (PCL) with paclitaxel (PTX) and magnetic nanoparticles (MNPs). The PCL mesh releases PTX slowly for at least 6 weeks when tested in vitro. The synergistic anticancer effect is achieved upon excitation of the mesh with an alternating magnetic field because the MNPs within the nanofiber generate localized heat which causes heat – induced cell killing as well as enhanced chemotherapeutic effect of PTX (Fig. 1). Based on these results, the smart nanofiber system may be very promising for cancer therapeutics in the future and may provide knowledge for new development of localized drug delivery.

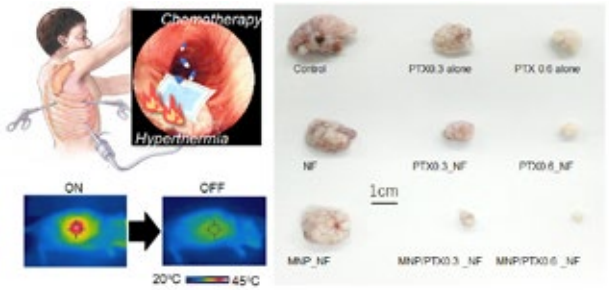

Fig. 1. IR thermal images of skin surface at subcutaneous tumor area in mouse transplanted with the MNPs-incorporated nanofiber mesh heated by an AMF (left), and ex vivo images of tumors retrieved from tumor-bearing mouse after 60 days of the treatment (right).

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Medical Soft Matter Group

Non-Equilibrium Dynamics of Pharmaceutical Glass

Group Leader
Kohsaku KAWAKAMI

Keywords: Pharmaceutical Glass,
Non-Equilibrium Dynamics

1. Outline of Research

Amorphous solids can offer higher solubility and dissolution rates in aqueous media relative to crystals. Thus it can be used for improving oral absorption of poorly soluble drugs.[1] However, the number of marketed oral amorphous formulations is still small. We are investigating non-equilibrium dynamic behaviors of pharmaceutical glasses to provide deeper understanding on their solid-state stability and supersaturation behavior after their dissolution.

2. Current Topics

Structure of glasses significantly depends on their thermal history. For example, experience of nucleation temperature lowers energetic barrier for crystallization,[2] although it is difficult to detect formation of nuclei. It is widely recognized that cooling rate from the supercooled liquid state influences energy state of the glass. Thus, we have investigated effect of the cooling rate on stability of the glass.[3] Fig. 1(a) shows effect of the cooling rate (q) on reversing heat capacity curves in the glass transition region for curcumin glass. Obviously, the glass transition temperature (T_g) increased with decreasing q. Sensitivity of the glass structure on q depended on the compound species. The slope of the T_g -ln$q$ plot for 12 pharmaceutical glasses was presented as a function of number of rotatable bonds in Fig. 1(b) to find good correlation except the data for ritonavir glass. Its exceptional behavior can be explained by stabilization by many hydrogen bonds and its large molecular weight. Thus, structural freedom appeared to be an important factor for the stabilization of the glass structure during the slow cooling.

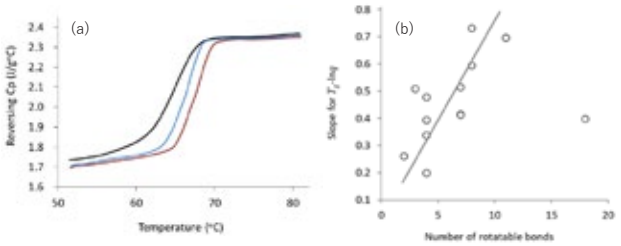

Fig. 1: (a) Reversing heat capacity ($\triangle Cp$) curves of curcumin glass prepared by cooling the melt at 20 °C/min (black), 0.1 °C/min (blue) and 0.05 °C/min (red). (b) Relationship between the slope for the *Tg -lnq* fitting and the number of rotatable bonds.

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Mechanobiology Group

Materials for Cellular Mechanobiology

Keywords: Mechanomedicine, Mechanobiology

Group Leader
Jun NAKANISHI

1. Outline of Research

Mechanobiology is a discipline that studies the role of physical force in life phenomena. Recent studies in this field shed light on the significance of force, comparable to chemical and biochemical cues, in the regulation of various biological and pathological processes. Our group develops various materials for understanding fundamental mechanobiology as well as for tissue engineering and drug screening applications based on the three concepts: (i) stimulus-responsive materials,[1] (ii) dissipative materials,[2] (iii) nano-confinement materials.[3]

2. Current Topics

Epidermal growth factor (EGF) is a protein that induce cell proliferation upon binding to the corresponding receptor (EGFR). Interestingly, however, it acquires contradictory apoptotic activities upon conjugation with gold nanoparticles (GNPs) through hitherto unknown mechanisms. We have identified an essential role of membrane rafts, nano-scale phase-separated domains in the plasma membranes, in the drastic activity switching of EGF-GNPs by confining the activated EGFR within the membrane rafts, eventually, changing the downstream phosphorylation cascades, i.e., extracellular signal-regulated kinase and AKT (Fig. 1).[3] Importantly, the destruction of membrane rafts by β-cyclodextrin reversed the signaling, restoring EGF-GNPs to lost anti-apoptotic property. These results reveal the importance of GNP-mediated signal condensation at membrane rafts in conferring the unique apoptotic activity on EGF-nanoparticle conjugates.

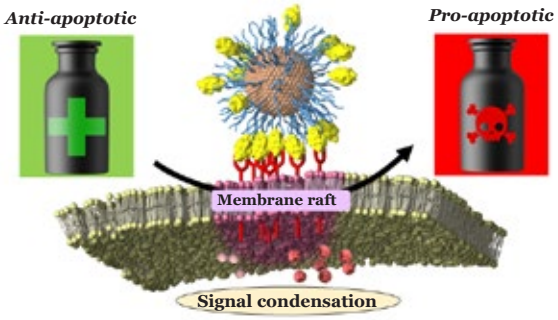

Fig. 1. Schematic representation of the role of membrane rafts for the activity conversion of EGF-GNP conjugates from proliferative to apoptotic at membrane rafts through signal condensation mechanisms.

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Surface Quantum Phase Materials Group

2D Superconductivity in Molecule-based van der Waals Heterostructures

Keywords: Superconducting heterostructures, Organic molecules

Group Leader
Takashi UCHIHASHI

1. Outline of Research

Recent advancement in nanotechnology has led to the extensive studies on atomic-layer materials such as graphene and transition-metal dichalcogenide. We successfully demonstrated the existence of 2D superconductivity by growing epitaxial indium atomic layers on a silicon surface through electron transport measurement.[1] This finding has stimulated researches of 2D superconductivity using a variety of 2D materials.

2. Current Topics

We have proposed molecule-based van-der-Waals 2D heterostructures consisting of a superconducting atomic-layer crystal and an epitaxially grown organic molecular layer (Fig. 1, left). Here each layer retains its intrinsic properties while the interlayer coupling can tune the 2D superconductivity. It is also expected to induce emergent physical phenomena such as topological superconductivity and new functionalities. Recently, we have created such 2D van-der-Waals heterostructures consisting of a superconducting indium atomic layer and three kinds of magnetic phthalocyanines (Pc), *i.e.*, CuPc, FePc, and MnPc. Superconductivity was found to persist in the presence of spin magnetic moments of a closely packed FePc layer and its exchange-interaction with conduction electrons (Fig. 1, right).[2] This is in marked contrast to the strong suppression of superconductivity by MnPc, which has magnetic properties analogous to those of FePc. The origin of the distinctive behaviors of these three molecules is attributed to the competition among superconductivity, magnetism, and the Kondo effect. The result indicates importance of subtle balance between the charge transfer and the exchange interaction between the two layers.

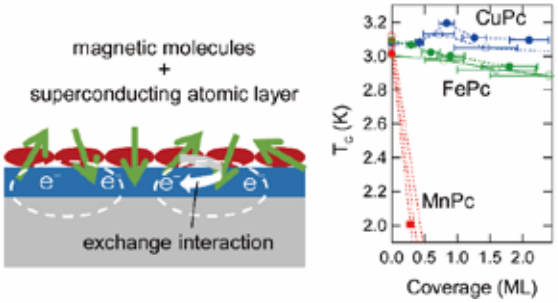

Fig. 1. (Left) Schematic illustration of the molecule-based 2D heterostructure. (Right) Coverage dependence of superconducting transition temperature (Tc) for the three kinds of molecules.

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Nanomechanical Sensing Group

Nanomechanical Sensing for Pattern Recognition of Solid Materials

Keywords: Mobile olfaction, Nanomechanical sensing

Group Leader
Genki YOSHIKAWA

1. Outline of Research

Demands for new sensors to detect or identify target molecules are rapidly growing in various fields; agriculture, food, medicine, security, environment, cosmetics, etc. Although nanomechanical sensors have potential to contribute to these challenges, it is still required to improve their performance in both hardware and software, especially receptor coating, which is a key to realizing actual applications.

2. Current Topics

Pattern Recognition of Solid Materials. In this study, we proposed that nanomechanics can be also utilized for pattern recognition of solid materials through a reverse approach; gaseous molecules as probes and solid materials as targets.[1] We have demonstrated that this approach can discriminate polymers with different molecular weights as well as those having slightly different functional groups evaluated through detailed classification using a support vector machine in addition to principal component analysis and linear discriminant analysis (Fig. 1). Classification of those target solid materials with 100% accuracy has been

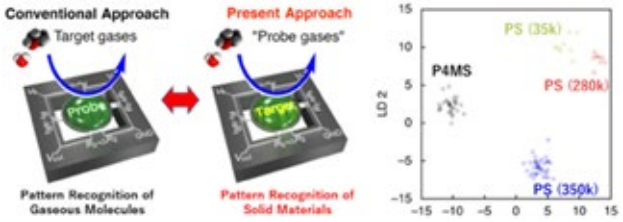

Fig. 1. Comparison between conventional and present approaches. An example of the identification of molecular weights of polymers.

achieved with some specific combinations of probe gases. Since any kind of gaseous molecule and any type of chemical sensor can be utilized as a probe and a sensing platform, respectively, this approach possesses unlimited possibilities to differentiate solid materials in various conditions, including the screening of receptor coatings on a sensor platform. Moreover, the target is not limited to a simple material but includes a complex mixture of functional materials, natural products, and various thin-film devices as long as gaseous molecules can interact.

Reference

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MANA Satellite

Emergent Dynamics of Neuromorphic Nanowire Networks

Keywords: Silver nanowires, Emergent dynamics

Principal Investigator
James K. GIMZEWSKI
(MANA Satellite at CNSI, UCLA, USA)

1. Outline of Research

We measured and analyzed emergent dynamics of PVP coated silver nanowires self-assembled into a network of resistive switchable electrical junctions creating a novel neuromorphic system. Electrical measurements across the network, reveal critical activation at a threshold voltage and evolution to optimal conductance states with successive cycles. A new measurement scheme reveals complex network dynamics arising from multi-scale interactions of the switch junction which have nonlinear and fading memory suitable for reservoir computation.[1]

2. Current Topics

Randomly self-assembled PVP-Ag nanowire networks were created by drop-casting onto SiO_2 substrates. Activation threshold of these networks and the role of resistive switching of single nanowire-nanowire junctions in the electrical properties has been studied (Fig. 1). In this work the spatio-temporal correlations were studied using power-laws of the power spectral distribution (PSD) of the network using multiprobes. Dynamical processes exhibiting these power-laws are present in systems with self-organized criticality (SOC) similar to those found in fMRI brain dynamics. Current-time series acquired on networks show dynamical fluctuations and evolution during the time series. These were compared with an electrical

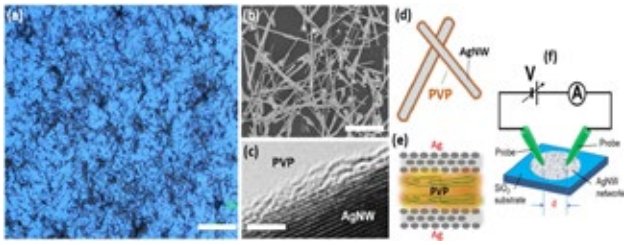

Fig. 1. Morphological and structural properties of PVP-coated Ag nanowires and nanowire network.

model of the network. Network activation was achieved under a constant bias voltage. Rather than a continuous transition, we observed a series of discrete current discontinuities. Our model indicates that resistive switching in specific topological areas of the network produced this effect. In the absence of bias voltage, network memorization occurs for varying periods of time. Stochastic dissolution of individual nanowire-nanowire junctions and the formation of multiple conductance pathways during the activation is combined with the model to explain this property.

Reference

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MANA Satellite

Surface Atomic Scale Logic Gate

Principal Investigator
Christian JOACHIM
(MANA Satellite at CEMES, CNRS, France)

Keywords: Molecule logic gates, Molecule machinery, Nano-car Race

1. Outline of Research

The Pico-Lab CEMES-CNRS Toulouse MANA satellite is working on the experimental and theory of QHC logic gates design, their current intensity drive, their mechanical inputs and by extension on single molecule machinery: molecule-gears, -motors, -nano-cars. The complexity roadmap is explored to master the emergence of a maximum quantum calculation power inside a single molecule or on passivated semi-conductor surface.

2. Current Topics

Quantum Hamiltonian Computing (QHC) is our recent approach using a single quantum system, in particular a single molecule, to perform computational tasks. This year, we have invented an explicit method to construct QHC complex Boolean logic gates where the logical outputs are encoded at fixed energy with a spatial positioning of the output quantum states or at different energies. We have constructed quantum Boolean adders involving a minimal number of quantum states: 8 quantum states for 3 inputs - 2 outputs Boolean adder. We also established a matrix algebra giving an analogy between classical Boolean logic gates and quantum ones without qubits and assess the possibilities of both designs for more complex gates than a 2 x 2 digital adder.[1] In mechanics, we have constructed molecule per molecule the first train of single molecule-gears able to transfer a rotation from one molecule-gear to the next (Fig. 1).[2] The nanofabrication of gold solid state nano-gear on sapphire down to a diameter of 30 nm was performed using the NIMS HIM machine to prepare the mechanical interconnection between a single molecule machinery and solid state nano-gears. Nano-car Race II for 2021 was actively prepared by the Toulouse MANA Satellite with now 10 teams registered coming from all the continents including the new MANA-NIMS team representing Japan.

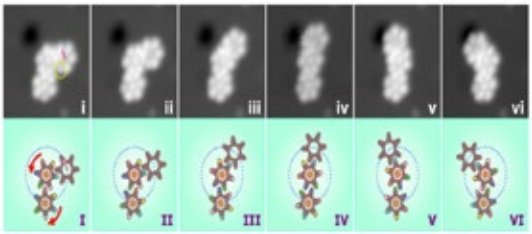

Fig. 1. The transmission of rotation along a molecule-gear train with its i-vi sequence of experimental STM images during a step-by-step Rotation and its model I-VI coming from ASED+ calculation.

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MANA Satellite

Nanoarchitectonics-Driven Functional Nanoparticles and Interfaces

Principal Investigator
Françoise M. WINNIK
(MANA Satellite at University of Helsinki, Finland)

Keywords: Photo/thermo/pH-responsive active matter, Functional nanoparticles

1. Outline of Research

Our research aims to design and fabricate responsive soft nanoparticles of controlled chemistry and morphology with possible applications as diagnostic tools and phototropic delivery agents.

2. Current Topics

Aqueous dispersions of nanogels that respond to switches in environmental pH or/and temperature by changes in their hydrodynamic radius (Rh) and/or ζ-potential were obtained and labeled with photochromic spiropyran (SP) moieties. Upon UV irradiation, the neutral SPs isomerize to the zwitterionic merocyanine (ME)s and upon UV light irradiation, the microgels formed by assembly of SP-nanogels undergo a collective motion toward the light source (Fig. 1).[1] Azopyridine (AzPy) groups affect the behavior of thermoresponsive polymers in response to three orthogonal triggers: pH through changes in ionization; light via trans-cis photoisomerization; and time, from hours to a few ms, via the kinetics of the dark cis-trans relaxation of AzPy.[2] These properties lead the way to responsive sensors or actuators in the form of aqueous fluids, hydrogels, or films by application of light and changes of temperature and pH in permutable sequences.[3]

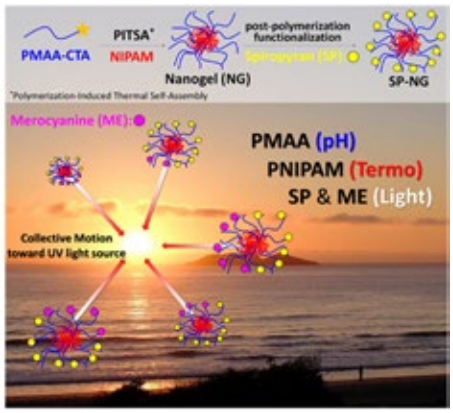

Fig. 1. Synthesis and phototropic motion of spyropyran-labeled microgels.

References

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Managing Researcher

Materials for Functional Nanomedicine

Keywords: Coating materials for medical devices, Implanted medical devices

Managing Researcher
Hisatoshi KOBAYASHI

1. Outline of Research

In general, organism selected quite limited molecules such as amino acids, lipids, sugar moieties, and limited metals and inorganics, and combined the limited molecules and finally constructed such highly functionalized complex systems. From the structure point of view, the organism is constructed by various nano-fibers and nano-particles under the highly dimensionally controlled condition. We mimic this system to create highly functional biomaterials for several applications.

2. Current Topics

Corneal transplantation is normally performed for treatment of the patient in a loss of eyesight by corneal disease. But the grafts self-supply rate in Japan is approximately 0% and lacks a cornea for transplant absolutely is reported by WHO. In the previous study, we have developed decellularized corneal stroma as the scaffold for corneal regeneration using ultrahigh hydrostatic pressure (HHP) method.[1-4] But there are still reformability about the transparency of its initial product and the shelf life. In this year, we tried to develop the new corneal decellularized stoma that was improved initial transparency and extended shelf life. The decellularization process of corneal stroma to make transparent graft was based on the freeze-drying. As shown in Fig.1, improvement of transparency was confirmed on the decellularized sample treated by low molecular weight chemical reagent which has polyvalence hydroxyl group.

(a) HHP-treated cornea
(b) Preservation outlook of transparent treated cornea

Fig. 1. Outlook of improved samples.

References

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Independent Scientist

Data Analysis Methods Toward Artificial Olfaction

Keywords: Machine learning, Gas sensors

Independent Scientist
Gaku IMAMURA

1. Outline of Research

Development of data analysis methods for gas sensor signals is essential for realizing practical artificial olfaction. By combining a data-scientific approach with MEMS-based gas sensor systems, I develop new analysis methods that can identify odors—complex mixtures of gases.

2. Current Topics

Olfaction is the only human sense that has not been realized as a practical sensor. In this study, a novel data analysis method based on transfer function ratios (TFRs) is proposed. Based on TFRs, one can identify odors without controlling or monitoring gas flow, leading to the free-hand measurement; the odor of a sample was measured by manually moving a small sensor chip—membrane-type surface stress sensors (MSS)—near the sample (Fig. 1a).[1] Odors of spices were measured with an MSS chip through the free-hand measurement. From the measurement data, TFRs were calculated. A result of principal component analysis on the TFRs shows the formation of clusters for each odor (Fig. 1b). A machine learning model based on random forest was developed, resulting in a classification accuracy of 0.89±0.04.

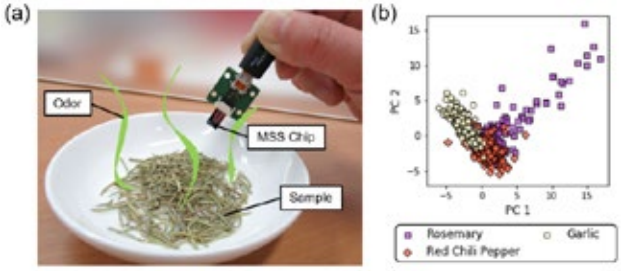

Fig. 1. (a) Picture of the free-hand measurement. (b) PCA scatter plot of TFRs.

Reference

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Independent Scientist

Large Diamagnetism in Organic Dirac Fermion System

Keywords: Dirac fermions, Magnetic susceptibility

Independent Scientist
Takako KONOIKE

1. Outline of Research

Since the discovery of graphene, it has been attracting a great deal of interest because the electrons in graphene behave like massless Dirac fermions. It is now become evident that Dirac fermion is realized not only in graphene, but also in various materials. In particular, organic conductor α-$(BEDT\text{-}TTF)_2I_3$ is known to be a first bulk crystal of Dirac fermion system. By taking advantage of its bulk nature, we experimentally study the physical properties of Dirac fermions in this organic compound.[1)]

2. Current Topics

The anomalously large diamagnetism in bismuth has been clarified that the "inter-band effects of magnetic field" plays an essential role in Dirac fermion systems.[2)] Contrary to the conventional theory, this effect enables the electrons cross between the two Bloch bands, without confining in particular band in weak magnetic field. In other words, virtual pairs of electron and hole caused by the vector potential perform orbital motion, which result in the large orbital diamagnetism. Theoretically, graphene is also expected to show a large orbital diamagnetism, though the clean single crystal is too small to detect the intrinsic nature of massless Dirac fermions. Here, we study the magnetic properties in organic Dirac fermion system. At ambient pressure, this compound undergoes semimetal to insulator transition at 135 K accompanied by charge ordering (CO). The charge ordered phase is suppressed by applying a pressure, and then turns into the massless Dirac Fermion (DF) phase above 12kbar. Recently, in between the charge ordered and massless DF phase, it was shown that there is the massive DF phase as an intermediate phase. In our measurements, we clearly detected the large diamagnetism in the three phases for the first time (Fig. 1). The possible origin of the large diamagnetism is the inter-band effects of magnetic field.

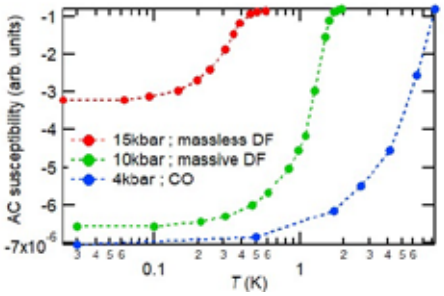

Fig.1. AC susceptibility vs. tempareture.

References

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Independent Scientist

Microbial Transmembrane Electric Conduit

Keywords: Heme, Flavin, Electrogenic Bacteria

Independent Scientist
Akihiro OKAMOTO

1. Outline of Research

Transmembrane multi-heme c-type cytochrome (OMCs) complexes function in unison as a biological "electron conduit" to transport electrons 20 nm or more across the outer membrane to the cell exterior in several genera of iron-reducing or -oxidizing bacteria (Fig. 1). The ability of the multi-heme alignment and interaction to promote highly efficient long-range electron transport under non-equilibrium conditions has been a focal point for nanoscale electronic, and bioenergy applications, and microbially influenced iron corrosion.

2. Current Topics

Given that the rate of EET – mediated by multiple heme redox centers (Fig. 1) – is significantly increased in the presence of flavins and quinones,[1)] such rate enhancement mechanisms (including molecule redox potentials and interactions) have been extensively studied. However, due to the structural similarity of these small molecules, it remains unclear how they are able to exert significantly differential effects (varying by factors of 100 or more) on EET rate enhancement. We reported the whole-cell electrochemical analysis of six flavin analogues and four quinones, demonstrating that protonation of the nitrogen atom at position 5 (N(5)) of the isoalloxazine ring is critical for electron outflow acceleration when flavins and quinones serve as a non-covalent cofactor of *Shewanella oneidensis* MR-1 OMCs.[2)] Upon calculating N(5) pKa (using a quantum chemical approach) and observing the impacts of the kinetic isotope effect (KIE) and pH change on measured current, we concluded that the extent of N(5) protonation controls the associated electron transport rate. As electron free energy has been a focal point in EET mechanisms, directly linking EET kinetics to the basicity of N(5) provides a basis for the development of novel strategies for controlling EET-associated biological reactions.

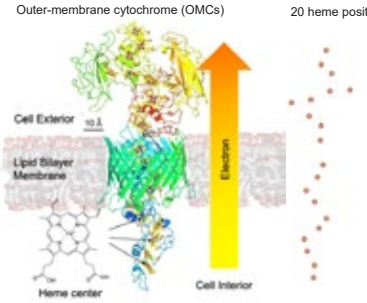

Fig. 1. Transmembrane multi-heme *c*-type cytochrome (OM *c*-Cyt) complex with 20 heme redox centers in *Shewanella oneidensis* MR-1.

References

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Independent Scientist

Shape Memory Polymer for Future Biomedical Applications

Keywords: Functional Shape Memory Polymer, Mechanobiology

Independent Scientist
Koichiro UTO

1. Outline of Research

My research aim is development of functional shape memory polymers (SMPs) for future biomedical applications. The research approaches include design and synthesis of new material system based on nanoarchitectonics concept. Particular attention is to develop functional SMPs with body-temperature, light irradiation, and other remotely controllable triggering (Fig. 1). In my current research, I have focused on its applications on mechanobiology studies.

2. Current Topics

The idea of material-based 'dynamic' mechanobiology is to mimic the living human body and it will break ground in this field, this concept contribute to basic study of molecular biology and application studies of drug discovery/screening by using more physiologically recapitulating cellular disease models.[1] In order to evaluate the potential of cultured cells to respond dynamic changes in vitro microenvironment, as they do in vivo, I have designed a novel shape memory cell culture platform that is capable of tuning surface topography mimicking dynamic cellular environment including extracellular matrix (ECM) and tissue remodeling. I have successfully demonstrated that the developed SMP cell culture platform has a potential to be a powerful tool to investigate the effects of patiotemporally presented mechano-structural stimuli on cell function and fate.[2] Given the importance of dynamic nature inside the body, SMP-based mechanobiology study may have important implications for advancing cellular functions and fate in vitro, as well as improving our understanding of cellular development in response to dynamic mechano-structural cues.

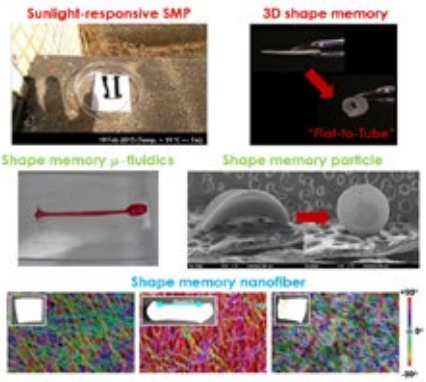

Fig. 1. Photographs of functional shape memory polymer with different architectonics.

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ICYS WPI-MANA Researcher

Quantum Transports in Graphene Superlattices for Spin-Valleytronics

Keywords: van der Waals Heterostructures, Valley Hall Effects

ICYS WPI-MANA Researcher
Takuya IWASAKI

1. Outline of Research

A concept to manipulate valley degrees of freedom instead of charge, has been proposed. This is called Valleytronics, expected for low power consumption device applications and quantum information processing. A key for development of Valleytronics is electrical control of the valley current, can be realized in graphene/hexagonal boron nitride (hBN) heterostructures aligned the crystal axis each other, forming a moiré superlattice (Fig. 1a). The superlattice strongly modifies the energy band structure of graphene, which provides a playground of fractal physics.

2. Current Topics

To fabricate the high-quality superlattice devices, a bubble-free transfer technique is developed. In this technique, a large bubble-free area can be obtained by using a polymer stamp with a protrusion at its center. The protrusion leads to form a hemispherical surface of the stamp, which support to define a finite contact angle between two-dimensional (2D) materials. With control of the contact speed and the substrate temperature, interfacial contamination is squeezed out from the 2D material stack during the transfer process. Thanks to the development of the transfer technique, high-quality bilayer graphene/hBN superlattice devices have been realized.[1] In the low temperature transport measurements, the quantum Hall effect with the fractal pattern, so-called Hofstadter's butterfly spectrum is observed (Fig. 1b). Moreover, the device shows the giant non-local resistance at zero field. By further analysis, we find that this resistance can be attributed to the topological valley current due to valley Hall and its inverse effects (Fig. 1c). In summary, the bubble-free transfer technique is indispensable for fabricating high-quality 2D heterostructures. The demonstration of valley Hall effects in the bilayer graphene superlattice system paves a way for development of functional Valleytronics devices in future.

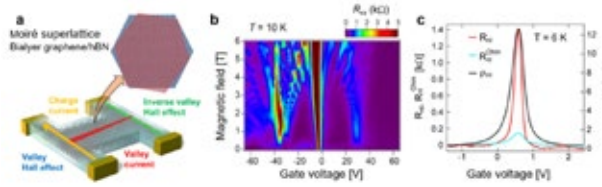

Fig. 1. (a) Schematic superlattice device and the valley Hall effect. (b) Hofstadter's butterfly spectrum. (c) Non-local resistance.

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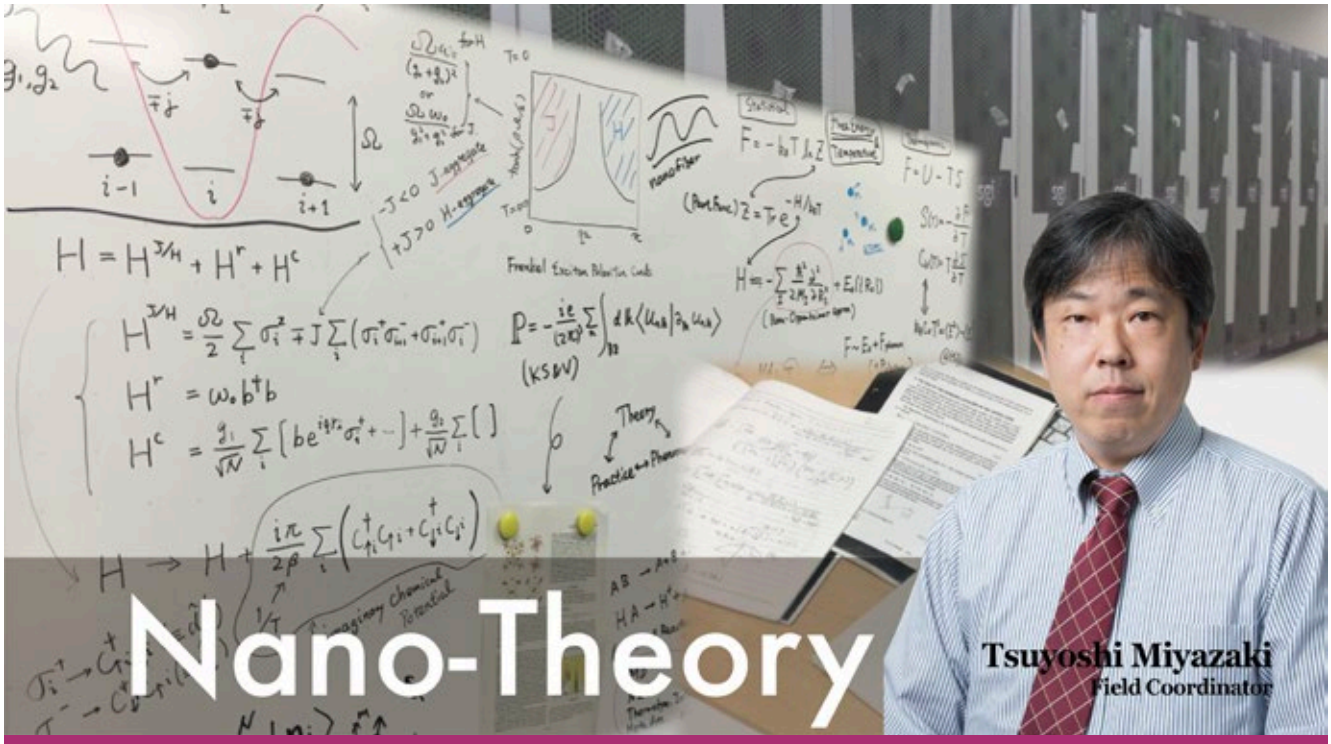

3 Research Groups

- **First-Principles Simulation Group**
- **Computational Nanoscience Group**
- **Emergent Materials Property Theory Group**

Understanding phenomena in the nanospace region, predicting new phenomena and creating novel nanostructured materials

Nanospace is a world in which common sense does not apply, where extremely small atoms are in motion, and electrons fly about in an even smaller space. Moreover, when huge numbers of these atoms and electrons act in coordination, they come to display behavior markedly different from those of single electrons and atoms. Ways of thinking and methods that are not bound by everyday common sense–namely, quantum mechanics and statistical mechanics–are essential for a proper understanding of the phenomena that occur there, and further, for devising new materials. Key activities in the field of nano-theory, which help achieve an understanding of the myriad phenomena emerging in nanospace, include building fundamental theories behind these novel behaviors by incorporating quantum mechanics and statistical mechanics, using our supercomputing facilities to obtain quantitative numerical predictions and develop new and efficient calculation methods. Besides providing interpretations of results obtained in other nanofield areas, we aim at invoking the outcomes of our research to predict as yet unearthed phenomena and to propose new materials featuring novel properties.

First-Principles Simulation Group

Theoretical Study of Nano-Scale Materials using Large-Scale DFT

Keywords: Large scale DFT code, Machine learning

Group Leader
Tsuyoshi MIYAZAKI
(Field Coordinator,
Principal Investigator)

1. Outline of Research

We develop new theoretical methods to calculate physical properties of complex nano-structured materials, including future electronic devices. Using the various developed theoretical methods, we clarify the dynamical processes in the formation of nano-scale structures and their exotic properties, in collaboration with the experimental groups in MANA. We mainly use first-principles calculation methods based on the density functional theory (DFT), but machine-learning techniques are also used to search new materials having given or preferable functions.

2. Current Topics

We have been developing a large scale DFT code CONQUEST, jointly with the group of Prof. David Bowler. CONQUEST has been already used in many areas,[1] but it is important for us to have more users and applications of the code. Since we are planning to open the code to public in this fiscal year, we have constructed pseudo atomic orbital (PAO) basis sets compatible with the widely used pseudopotential database, PseudoDojo. We have compared the results of small (SZP), medium (DZP) and large basis sets (TZTP) with the converged planewave calculations and demonstrated that the accuracy of large PAO basis set is almost the same as the results by planewaves.[2] We also developed analysis methods based on large-scale DFT molecular dynamics simulations. Using the methods, we have studied many systems, such as the interfaces of Si/Ge core-shell nanowires, SiO_2 melt at high temperature and pressures, formation of amorphous structures, core-shell metallic nanoclusters (Fig. 1(a)), and so on. In addition, machine-learning (ML) forces for the solid and liquid states of silicon and germanium were constructed from the training data generated by O(N) first-principles molecular dynamics simulations (Fig. 1(b)).[3]

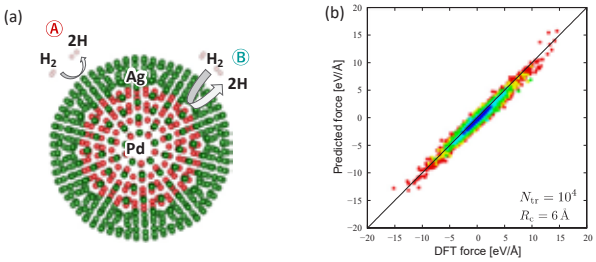

Fig. 1. (a) Pd@Ag core-shell nanoparticles. (b) Comparison between ML and DFT forces for solid and liquid Germanium.

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Computational Nanoscience Group

Theoretical Studies of Low Dimensional System

Keywords: First-principles Calculations, Two-dimensional sheets

Group Leader
Masao ARAI

1. Outline of Research

Our group investigates electronic structures and physical properties of bulk and nanostructured materials with theoretical and computational methods. Ultimate goal of our research is to understand exotic properties and predict nanomaterials with novel properties. Several graphene-like sheets and other low dimensional system were studied with theoretical methods including topological analysis and first-principles calculations based on the density-functional theory (DFT).

2. Current Topics

On the surface of ZrB_2, "siliborophene" Si_3B_6 was found from the combination of experimental and theoretical researches (Fig. 1).[1] Its detailed structure was elucidated from extensive first-principle calculations. The calculated phonon spectrum of candidate structure agrees well with that from EELS experiments. From the theoretical calculation of complex layered compound $Sc_2B_{1.1}C_{3.2}$, new type of graphene-like BC_2 sheet has been found. The stability of its structure was found to be related with electric charges of layers. The transition metal carbides, MXenes, which can be synthesized from MAX phase have been predicted to show various electronic structure and physical properties. Among them, W_2CO_2 has been predicted to be large gap topological insulator. We continued the search of topologically non-trivial band structure by calculating Berry curvature and Chern number for ferromagnetic materials.

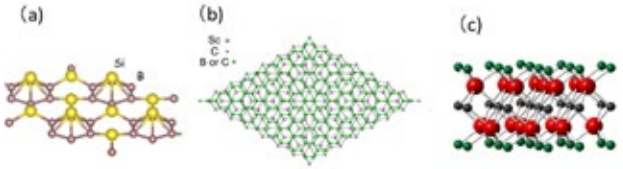

Fig. 1. (a) "Sliborophene" Si_3B_6. (b) $Sc_2B_{1.1}C_{3.2}$: layered structure composed of graphene-like BC_2 and MXene-like Sc_2C. (c) Surface functionalized MXenes.

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Emergent Materials Property Theory Group

Theoretical Quest for Emergent Materials Function

Keywords: Magnetic skyrmions, Topologically stable materials functions

Group Leader
Akihiro TANAKA

1. Outline of Research

We develop and integrate an assortment of theoretical methods powerful enough to zoom in on the behavior of the many-body system: first principle calculations, numerical schemes based on statistical mechanics, and nonperturbative (analytical) quantum field theory methods. Our primary aim is to extract from such studies novel material properties which can lead to resourceful quantum mechanical functions.

2. Current Topics

Currently there is an urgent demand for radically new information storage and processing means that will improve on the capacity, operating time scale and power consumption level that silicon based state-of-the-art technology offers. In recent years, a powerful candidate for such purposes has emerged: magnetic skyrmions, a topological spin structure realized in magnetic films, which are stable objects behaving in many ways like nanoscale particles. Research conducted in our group[1] now shows that skyrmions also act as sources of electric polarization. From an application perspective, this may e.g. open up the possibility of performing information processing involving skyrmion motion in a purely electrically controlled way.

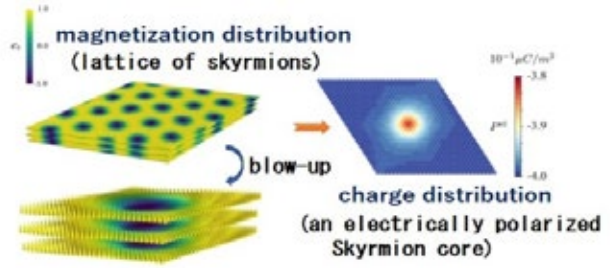

Fig. 1. Magnetization distribution of layered ferromagnetic material GaV_4S_8 in an applied magnetic field (left), and the charge distribution in the vicinity of the magnetic skyrmion core (right).

This multiferroic behavior was found in the quasi two-dimensional material GaV_4S_8 as depicted in Fig. 1, where the magnetization/electric polarization profiles were derived from an effective model extracted systematically from first-principle electronic states calculations. This scheme which seamlessly integrates microscopic and effective descriptions of quantum materials has a wide range of applications, and is also employed e.g. in our quest for materials exhibiting new topological phases.[2]

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Principal Investigator

Nano-System Computational Science

Keywords: DFT calculations, Interface

Principal Investigator
Yoshitaka TATEYAMA

1. Outline of Research

"Interface Ionics", ion dynamics and kinetics around interface, is essential for energy devices as well as electronic ones, while identifying or sampling of interface properties is still difficult in both experiments and calculations. To solve this issue especially for solid-solid interfaces, we have developed a new calculation technique to efficiently and accurately sample complex heterogeneous solid-solid interfaces. Together with other DFT calculation and AI techniques, we have clarified several microscopic mechanisms of batteries and catalysts.

2. Current Topics

All-solid-state battery (ASSB) is regarded as a promising next generation battery, whereas these devices contain many internal solid-solid interfaces, resulting in low ionic conductivity and instability. To improve their performance, the ionics mechanisms of these solid-solid interfaces need to be understood at the nano scale. However, it had been extremely difficult to determine electronic and ionic states at complex heterogeneous solid-solid interfaces (HSSIs).
For the first time in the world, we have developed a highly accurate, integrated calculation method "heterogeneous interface CALYPSO (crystal structure analysis by particle swarm optimization) method" (Fig. 1) that enables quantum and statistical analyses of HSSIs. This method allows

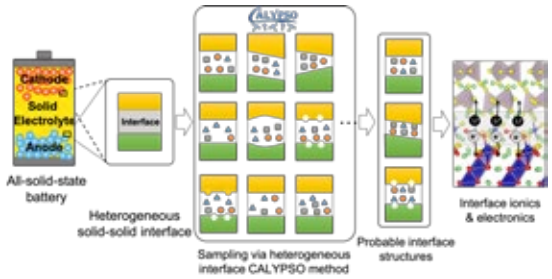

Fig. 1. A schematic flowchart of the Heterogeneous Interface CALYPSO method.

optimization of all degrees of freedom associated with local and collective relations at HSSIs, and combining CALYPSO technique for efficient structure predictions. It also involves DFT calculations for accurate prediction of structures. We applied this method to the interfaces between an oxide cathode and a sulfide electrolyte in sulfide-based ASSBs and theoretically demonstrated that combination of interfacial electron transfer and electrochemical reactions as well as dynamical depletion of interfacial lithium ions can cause low ion conductivity at the electrode-solid electrolyte interfaces.[1]

Reference

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Studies of Strain and Doping on Nanomaterials

Keywords: CONQUEST linear scaling DFT code, Applications in photovoltaic devices

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

1. Outline of Research

Our ultimate aim is to understand advanced nano-structured materials for applications in photovoltaic devices, as well as future electronic devices. 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.

2. Current Topics

We have continued our work on the growth and properties of silicon nanowires and germanium-silicon core-shell nanowires, in collaboration with Dr. N. Fukata in MANA, who grows the nanowires. We have studied the electronic structure of silicon nanowires, both pure and with As dopants (Fig. 1).[1] These simulations used the multi-site support function approach in CONQUEST, which allows us to model several thousand atoms exactly. We have also continued our work on the accuracy and ease of use of CONQUEST, with the full, open-source release of the code approaching. We have created a utility that uses a reliable, accurate set of pseudopotentials (from the PseudoDojo project) and automatically generates basis sets. For the largest basis sets, we have demonstrated that the accuracy

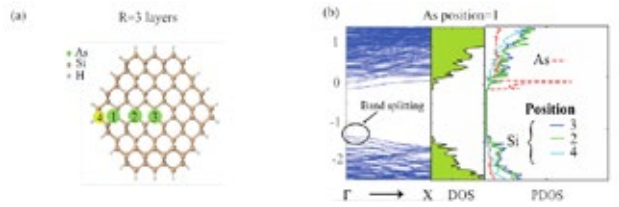

Fig. 1. (a) Comparison of band structure and density of states (DOS) of Si NWs with R = 3 layers and L = 8 layers, with the As dopant in different positions. (b) The band structure, DOS and the PDOS for position 1.

is comparable to completely converged plane wave calculations.[2] We are currently preparing the CONQUEST code for release, working on providing users with all the elements required to make the code usable (alongside the source code, a database of pseudopotentials, a manual, tutorials and a test suite). This will be a major deliverable from the long-term UCL-NIMS collaboration in the area of electronic structure, with calculations possible on systems from 1 atom to over 1,000,000 atoms.

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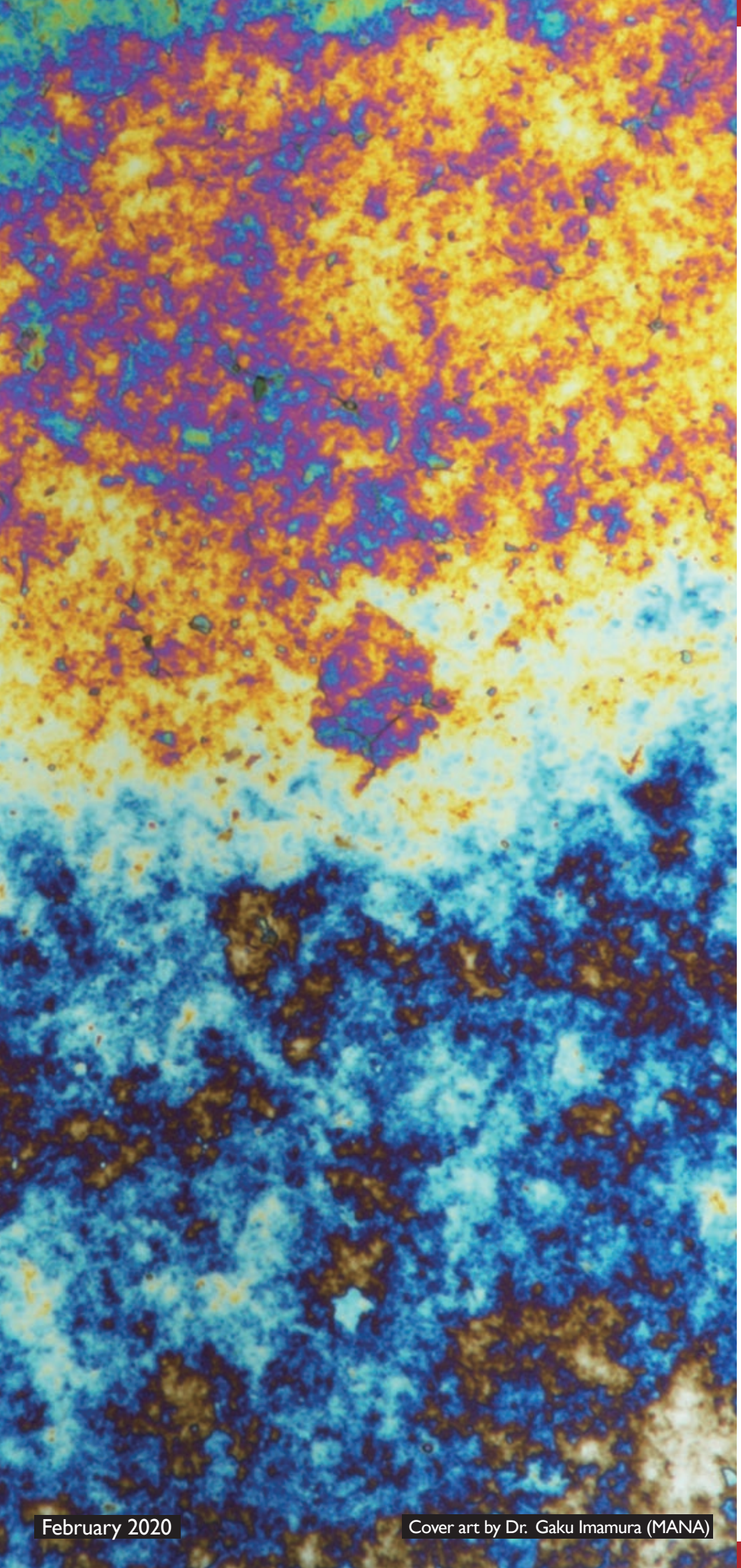

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