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World Premier International Research Center Initiative

MANA
Nano Revolution for the Future

Research at MANA

International Center for Materials Nanoarchitectonics

Twenty Selected Research Results

2007-2013

Message from the Director

MANA was launched in October 2007 as one of five research centers in the framework of the World Premier International Research Center Initiative (WPI) Program of Japan's Ministry of Education, Culture, Sports, Science and Technology (MEXT). As the director of MANA, I am happy to be able to announce that MANA has grown into a world-class research hub for the fields it handles in the seven years since it was launched. In fact, MANA's excellence is apparent from several statistical indicators that exceed those of many other world-class research institutions. For example: The number of papers in the world's top 1% by the number of citations has reached 80; MANA has achieved a very high (2.5) field-weighted citation impact (FWCI) -a new indicator devised by Elsevier to fairly compare the quality of papers published by research institutions in different fields; and,The average impact factor (IF) of journals in which MANA researchers have published their papers is very high, at 5.08.

MANA has a unique characteristic among the many research institutions focused on materials science around the world–namely, MANA operates on the basis of our unique concept of "nanoarchitectonics," a new paradigm of nanotechnology that will be explained in more detail on the next page. We recognize that this unique concept has been key to MANA's research achievements.

In the seven years since its launch, MANA has obtained many remarkable research results, from fundamental breakthroughs to applications. The purpose of this booklet is to select and compile 20 representative research results and briefly explain each of them. As shown on pages 6 and 7, the 20 examples can be grouped into three major categories: Creation of New Fields of Research, Fusion of Interdisciplinary Research Fields, and Other Remarkable Research Results.

It should be pointed out that these 20 examples are by no means the comprehensive list of MAMA's research results. Many other remarkable results have been obtained, and they will be included in a more comprehensive report in the future.

Masakazu Aono
Director,
International Center for Materials Nanoarchitectonics (MANA), National Institute for Materials Science (NIMS)

What is Nanoarchitectonics?

When MANA was established seven years ago in NIMS, Japan's primary research institution for materials science, nanotechnology (and its foundation, nanoscience) was progressing rapidly and fast becoming indispensable in the field of materials science. Against this backdrop, we designed MANA to create a world-class research center that could boldly promote the development of new materials through the effective use of nanotechnology. In designing the center, we were keenly aware that the true power of nanotechnology could not be harnessed without acknowledging that nanotechnology was fundamentally different from microtechnology, and that the prevailing view of nanotechnology as an extension of microtechnology was incorrect. In order to crystallize this notion, we proposed the concept of "nanoarchitectonics". Nanoarchitectonics is a new paradigm of nanotechnology, founded on four principles , as follows:

Nanoarchitectonics Key Principles

1 Create reliable nanomaterials or nanosystems by organizing nanoscale structures (nanoparts) which may have "some unreliability".

2 Note that the main players are not the individual nanoparts but their "interactions", which cause a new functionality to emerge.

3 Recognize unexpected emergent functionalities that can result from assembling or organizing a "huge number" of nanoparts.

4 Create a new theoretical field where conventional first principles computations are combined with novel "bold approximations".

Our Vision

Toward a better global future:

Pioneering a new paradigm in materials development using nanoarchitectonics concept

Our Mission

Develop ground-breaking new materials on the basis of the nanoarchitectonics concept

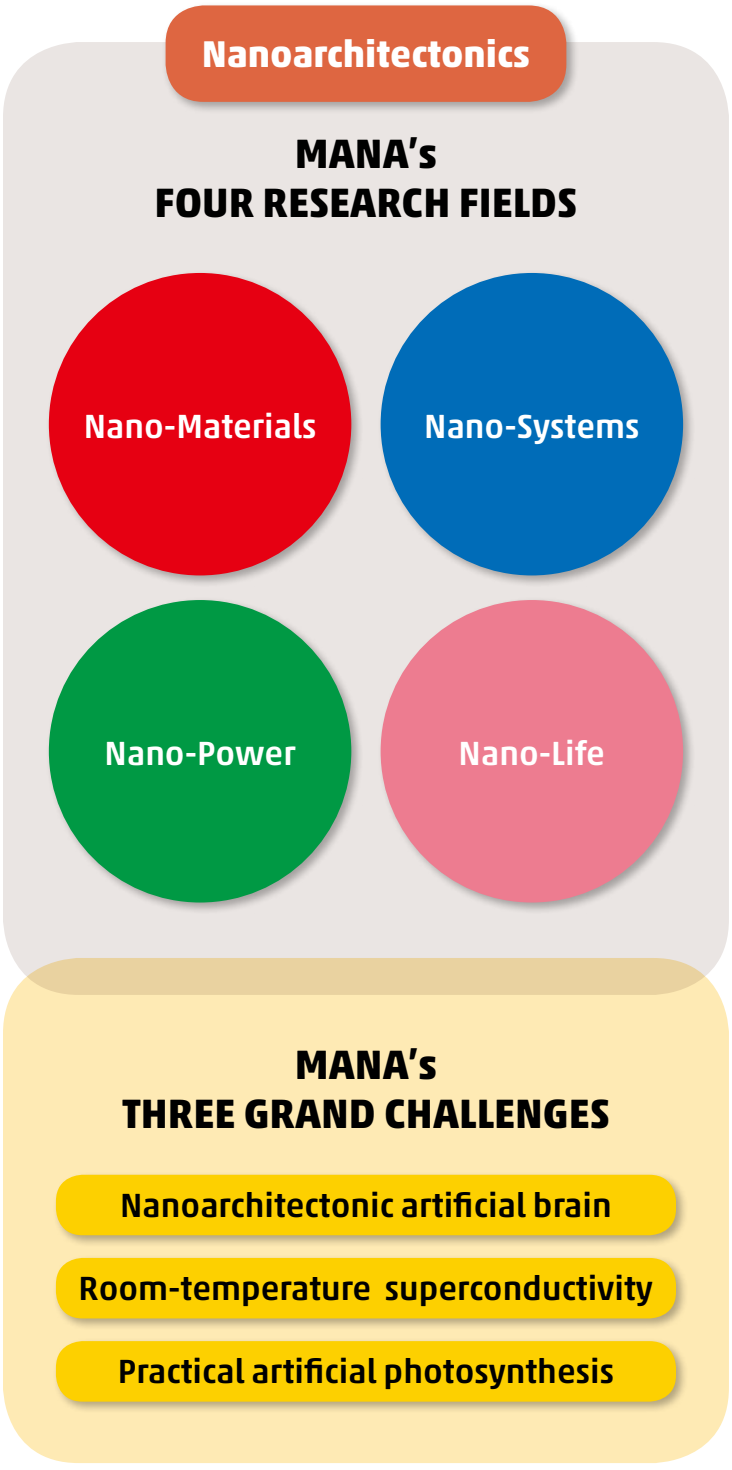
Create a "melting pot" where top-level researchers gather from around the world

Secure young scientists and foster their confidence to battle toward challenging targets

Construct a world wide network of nanotechnology centers

MANA's four Research Fields and three Grand Challenges

On the basis of MANA's vision and mission, as described on the previous page, we are pursuing research and development in four areas. In addition, we have identified three grand challenges to promote interdisciplinary work and a fusion of our four fields of research.



Research at MANA

Twenty Selected Research Results

2007-2013

Creation of New Fields of Research

Nanosheet-based Breakthroughs for Creating Novel Materials

01 Production of high-quality functional nanosheets via massive swelling/exfoliation of layered crystals

02 High-*k* oxide nanosheets: New 2D materials and devices beyond graphene

Atomic Switch and Related Prospective Devices and Systems

03 Atomic switch: Novel on/off switching characteristics and unique synapse-like behaviors

04 Atomic Switch Networks: A new approach to neuromorphic computation

Molecular-scale Site-designated Chemical Nanoarchitectonics

05 Electrical wiring of single molecules via conductive molecular chains

06 Controlling bound and unbound states of molecules (C_{60}) reversibly at designated sites

Fusion of Interdisciplinary Research Fields

Nanoarchitectonics-inspired Nano-life Science

07 Nanoarchitectonic smart nanofibers for cancer therapy

08 Novel nanoarchitectonic therapeutics –Complete recovery from Alzheimer's disease

Nano-life Science-inspired Nanoarchitectonics

09 Ultrasensitive and ultraparallel molecular sensing for use in artificial noses and other applications

10 Progress in high-efficiency artificial photosynthesis

Theory-Experiment 'Cross-linkage' for Exploring Novel Nanoscale Materials and Systems

11 Topological matter nanoarchitectonics for novel quantum devices

12 Ultra-large-scale computation: Development and application of an advanced code

Other Remarkable Research Results

Innovative Nanoscale Devices and Systems

13 Mesoscopic superconductivity quantum phenomena in superconductor and normal-metal junctions

14 Silicon-doped metal oxide thin film transistor for flat panel application

15 Nanogenerators and self-powered nanosystems

Innovative Nanoscale Characterization Methodologies

16 Multiple-probe scanning probe microscopes (STM, AFM, KFM): Development and Application

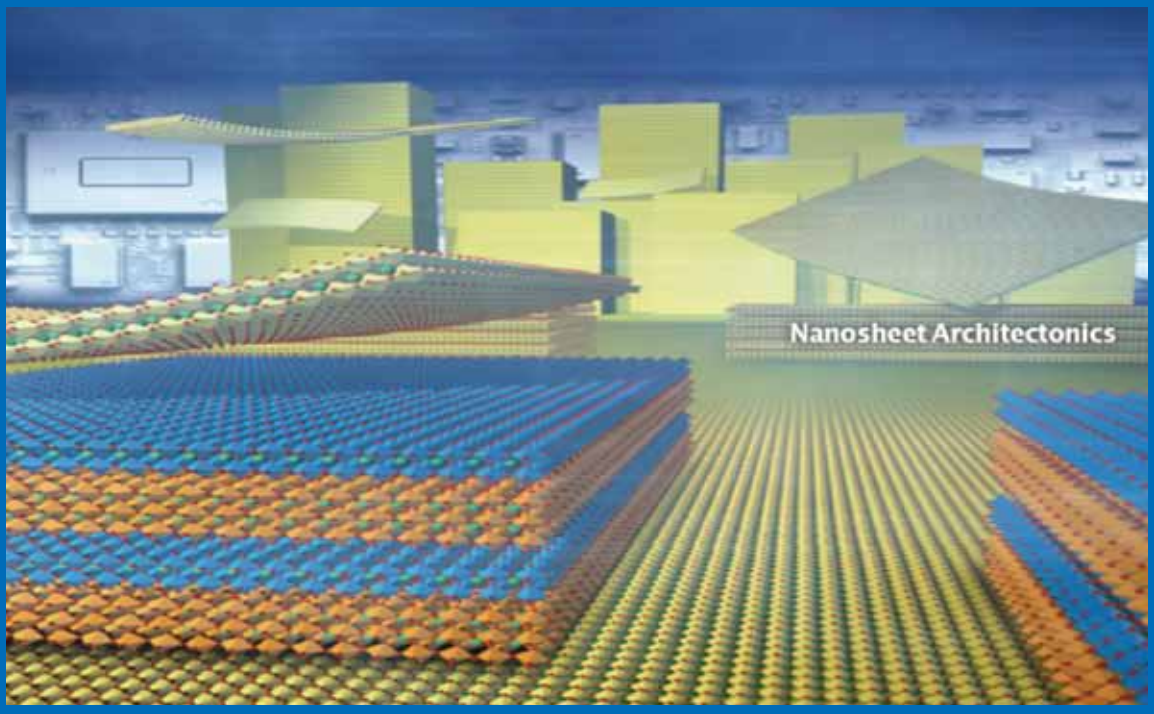
17 Pioneering development of *in situ* TEM techniques for nanomaterial property analysis

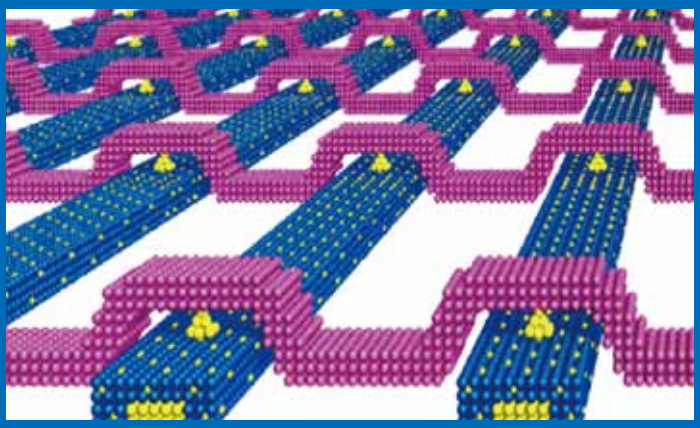
Nanoarchitectonics Related to Sustainable Energy and Environment

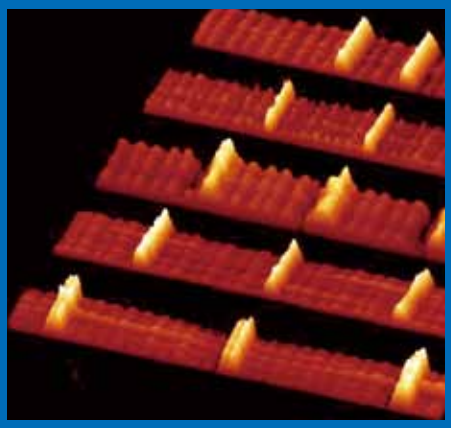
18 Novel porous materials for next-generation high-performance batteries

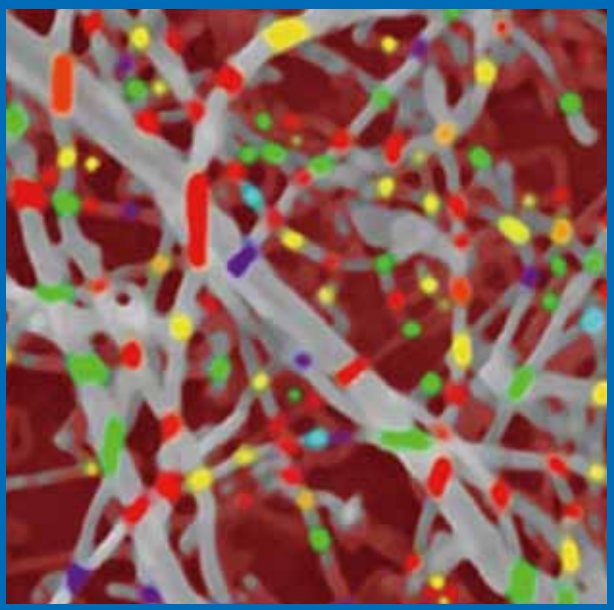
19 Nanoarchitectonic sensing and imaging of Cs in life environment

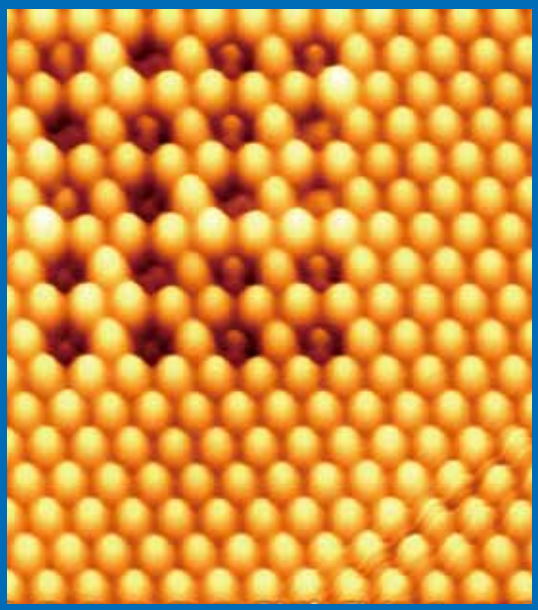
20 Highly-efficient plasmonic systems for molecular sensing and energy conversion


Nanosheet Architectonics









Creation of New Fields of Research

Nanosheet-based Breakthroughs for Creating Novel Materials

Atomic Switch and Related Prospective Devices and Systems

Molecular-scale Site-designated Chemical Nanoarchitectonics

01 Production of high-quality functional nanosheets via massive swelling/exfoliation of layered crystals

Representative researcher: **T. Sasaki**

Aquacrystals: New process yields superior nanosheets suitable for tailored products

We have developed a variety of oxide and hydroxide nanosheets via inducing enormous swelling of layered crystals in aqueous amine solutions. The extraordinarily expanded "aquacrystals" can be gently disintegrated into unilamellar nanosheets of high yield, which is difficult to attain by other delamination procedures. This process has been applied to various layered crystals synthesized in a tuned composition and structure to produce tailor-made nanosheets exhibiting unique and useful properties. The high-quality nanosheets thus obtained have been utilized as building blocks for "2D Nanosheet Nanoarchitectonics" to design functional nanostructured materials and nanodevices.

Molecularly thin two-dimensional (2D) nanomaterials, termed nanosheets, are of increasing interest owing to their novel properties and enormous applicability in fields ranging from electronics to catalysis. One efficient approach for producing nanosheets in high-quality is to expand the gallery of layered crystals by introducing guest molecules to weaken the interaction between neighboring layers. Recently, we attained the massive swelling of layered metal oxide crystals in a range of amine solutions. The crystals extraordinarily grew into an extended length beyond 200 μm (Fig.1). Small X-ray scattering analysis revealed the swollen structure with a maximum interlayer distance of 90 nm, i.e. 100-fold swelling from an original value of 0.89 nm (the right panel in the figure). In-depth characterizations indicate that the gallery is primarily occupied by H_2O molecules (Its content: >97 wt%). We found that the swollen "aquacrystals" are more stable when amines are smaller or more polar; while those swollen when amines are large or geometrically symmetrical are easily delaminated. These studies provide an important benchmark for controlled production of high-quality 2D nanosheets. We have applied this knowledge on the soft-chemical exfoliation to various layered crystals synthesized in a designed composition and structure to produce a range of oxide and hydroxide nanosheets exhibiting superior electronic, magnetic, optical and chemical functionalities. We have, thus, developed a 2D nanosheet library, or toolbox, which has been effectively utilized in "2D Nanosheet Nanoarchitectonics" for tailoring functional nanostructured materials and nanodevices.

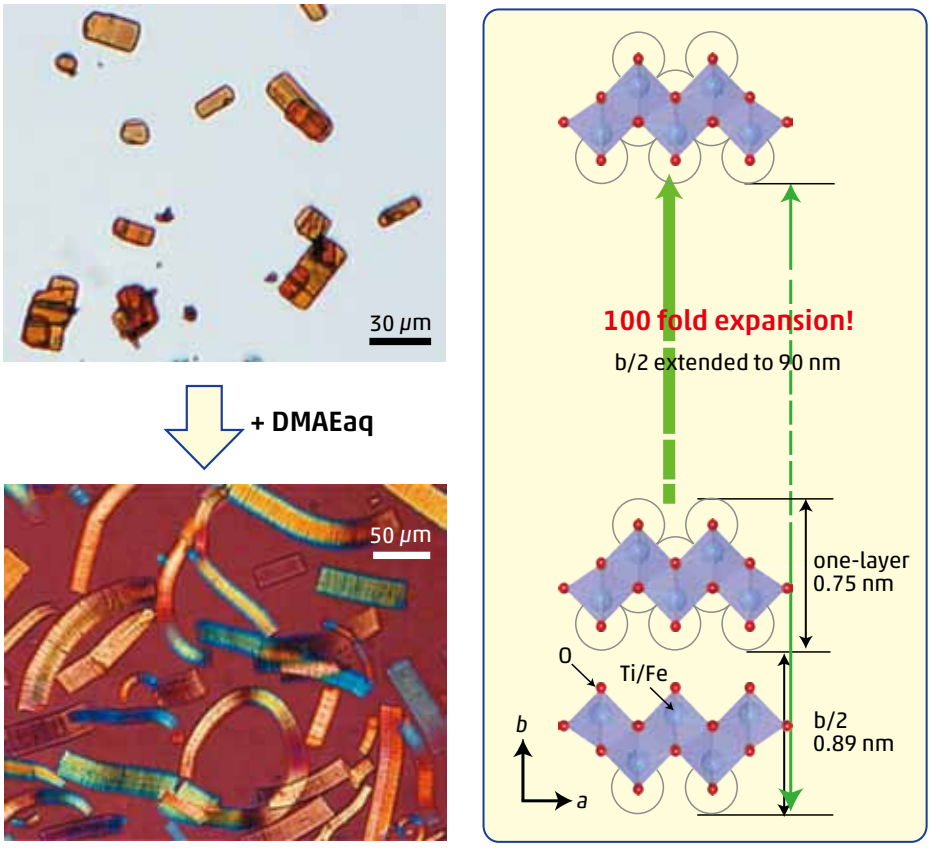


Fig. 1. Platy microcrystals of a layered titanate before and after the treatment with aqueous 2-dimethylaminoethanol (DMAE) (left). Structural illustration of the swelling (right).

Main papers

1) "Reversible, instant, and unusually stable ~100-fold swelling of inorganic layered materials", F. Geng, R. Ma, A. Nakamura, K. Akatsuka, Y. Ebina, Y. Yamauchi, N. Miyamoto, Y. Tateyama, T. Sasaki, *Nature Commun.* **4** (2013) 1632.
2) "Gigantic swelling of inorganic layered materials: A bridge to molecularly thin two-dimensional nanosheets", F. Geng, R. Ma, Y. Ebina, Y. Yamauchi, N. Miyamoto, T. Sasaki, *J. Am. Chem. Soc.* **136** (2014) 5491.
3) "Nanosheets of oxides and hydroxides: Ultimate 2D charge-bearing functional crystallites", R. Ma and T. Sasaki, *Adv. Mater.* **22** (2010) 5082.

02 High-*k* oxide nanosheets: New 2D materials and devices beyond graphene

Representative researchers: **M. Osada, T. Sasaki**

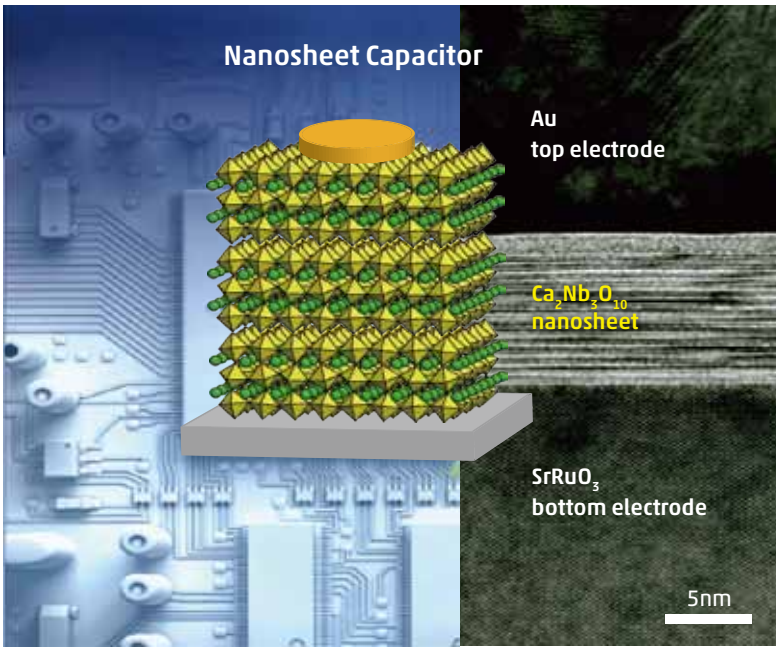
LEGO-like assembly: 2D oxide nanosheets open new route to high-performance electronic devices

We have developed high-*k* oxide nanosheets, an important material platform for ultra-scale electronic devices and post-graphene technology. The new nanosheets (Ti_2NbO_7, $(Ca,Sr)_2Nb_3O_{10}$) realized the highest permittivity (ε_r = 210–320) of all known dielectrics in the ultrathin region (< 10 nm). Layer-by-layer engineering of these nanosheets enabled us to design 2D dielectric devices that cannot be achieved in graphene and other materials. Graphene is only the tip of the iceberg, and we are now starting to discover new possibilities afforded by 2D oxide nanosheets.

Two-dimensional (2D) nanosheets with atomic or molecular thickness are emerging as important new materials owing to their fascinating physical properties. Despite significant advances in graphene-like 2D nanosheets, it remains a challenge to explore high-*k* dielectric counterparts, which have great potential in new 2D electronics. Oxide nanosheets may be the perfect solution as a new era unfolds in 2D dielectrics and post-graphene technology. We found that titania- or perovskite-based nanosheets exhibit superior high-*k* performance (ε_r = 210–320) even at a few-nm thicknesses (Fig.1), opening a new route to ultra-scaled electronic devices. Notably, nanosheet-based capacitors exhibited an unprecedented capacitance density (~100 μF/cm^2), which was 1,000 times higher than that of state-of-the art ceramic condensers. We also utilized high-*k* oxide nanosheets as building blocks in the LEGO-like assembly, and successfully developed various functional nanodevices such as nanosheet FETs, all-nanosheet capacitors, artificial ferroelectrics, etc. Our work is a proof-of-concept, showing that high-performance nanodevices can be made from "nanosheet-architectonics".

Main papers

1) "Two-dimensional dielectric nanosheets: Novel nano-electronics from nanocrystal building blocks", M. Osada, T. Sasaki, *Adv. Mater*. **24** (2012) 210.
2) "Controlled polarizability of one-nanometer-thick oxide nanosheets for tailored, high-*k* nanodielectrics", M. Osada, G. Takanashi, B-W. Li, K. Akatsuka, Y. Ebina, K. Ono, H. Funakubo, K. Takada, T. Sasaki, *Adv. Funct. Mater*. **22** (2011) 3482.
3) "Robust high-*k* response in molecularly thin perovskite nanosheets", M. Osada, K. Akatsuka, Y. Ebina, H. Funakubo, K. Ono, T. Sasaki, *ACS Nano* **4** (2010) 5225.
4) "Engineered interfaces of artificial perovskite oxide superlattices via nanosheet deposition process", B-W. Li, M. Osada, T. C. Ozawa, Y. Ebina, K. Akatsuka, R. Ma, H. Funakubo, T. Sasaki, *ACS Nano* **4** (2010) 6673.



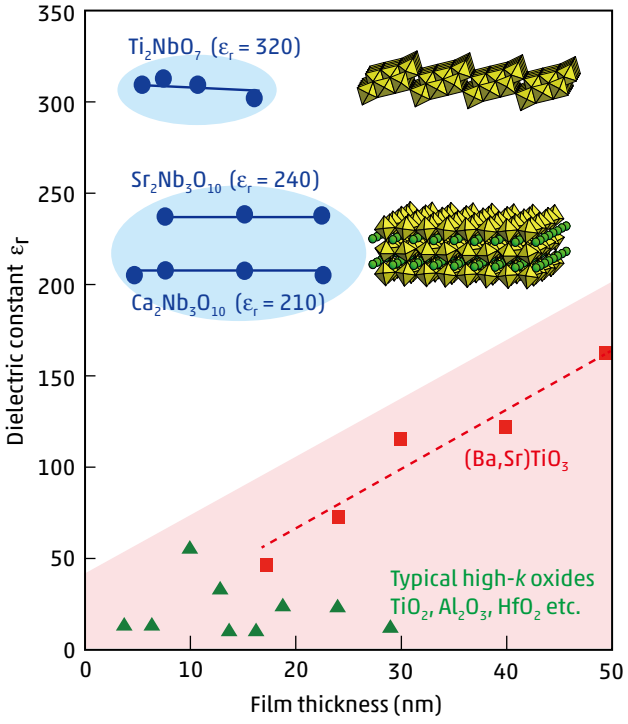


Fig. 1. Schematic illustration and TEM image of nanosheet-based capacitor (left). Dielectric properties of oxide nanosheets and various oxide thin films (right).

03 Atomic switch: Novel on/off switching characteristics and unique synapse-like behaviors

Representative researchers: **T. Hasegawa, K. Terabe, M. Aono**

Paradigm shift: Atomic switch enables novel developments in computing

We have developed a novel switching device having better characteristics than conventional semiconductor transistors in that it is a non-volatile switch having smaller dimensions and lower energy consumption. The unique operating mechanisms of the atomic switch--movement of metal atoms/ions associated with their redox processes due to an applied potential--have enabled the development of various novel functions, such as non-volatile three-terminal operations and synaptic operations.

The novel characteristics of the atomic switch make it a universal switch, which can be used in various applications, such as, memory, logic, neuromorphic systems, etc. In the applications, atomic switches not only improve the performance of present-day computing systems, but also enable development of conceptually new electronic systems. For instance, the atomic switch has enabled the development of the "Programmable CBIC (Cell-Based Integrated Circuit)", which has been one of the dreams in electronic industries since it enables all the functions and similar performance of ASICs (Application Specific Integrated Circuits) in a single device. Regarding application, we have already reached a technological level for the commercialization of advanced IC chips equipped with the atomic switches (in collaboration with NEC Corp.). Atomic switching has also achieved non-volatile three-terminal operation [1], drastically reducing the energy consumption of von Neumann computing systems, in which a 'volatile' semiconductor transistor is now a main element. By using various atomic switches, such as an 'on-demand function-selectable atomic switch' [2] and 'photo-sensing atomic switch', we can cause a paradigm shift in information technology. In this sense, the development of a 'synapse-like atomic switch junction' [3], illustrated in Fig. 1(a), is one of the most important results of atomic switch studies in the last decade. As Figs. 1(b) and (c) panels show, when we monitor the conductivity of the junction with an input voltage pulse applied repeatedly, if the frequency of the voltage pulse is low, the junction is not switched on even after many voltage pulses (Fig. 1(b)); but if the frequency is large enough, the junction is switched on after several voltage pulses (Fig. 1(c)). These are quite similar to two types of plasticity of the synapse in the human brain, i.e., short-term plasticity (STP) and long-term potentiation (LTP). These synaptic characteristics have been emulated using a CMOS circuit, where pre-programming and circuit designing determine everything, i.e., all the results. The results shown in Fig. 1, which were achieved by atomic switch itself, are of great interest in that they encourage us to develop conceptually new artificial neuromorphic computational systems that do not require pre-programming.

Main papers

1) "Volatile/nonvolatile dual-functional atom transistor", T. Hasegawa, Y. Itoh, H. Tanaka, T. Hino, T. Tsuruoka, K. Terabe, H. Miyazaki, K. Tsukagoshi, T. Ogawa, S. Yamaguchi, M. Aono, *Applied Physics Express* **4** (2011) 15204.

2) "On-demand nanodevice with electrical and neuromorphic multifunction realized by local ion migration", R. Yang , K. Terabe , G. Liu , T. Tsuruoka , T. Hasegawa, J. K. Gimzewski, M. Aono, *ACS Nano*, **6** (2012) 9515.

3) "Short-term plasticity and long-term potentiation mimicked in single inorganic synapses", T. Ohno, T. Hasegawa, T. Tsuruoka, K. Terabe, J. K. Gimzewski, M. Aono, *Nature Materials* **10** (2011) 591.

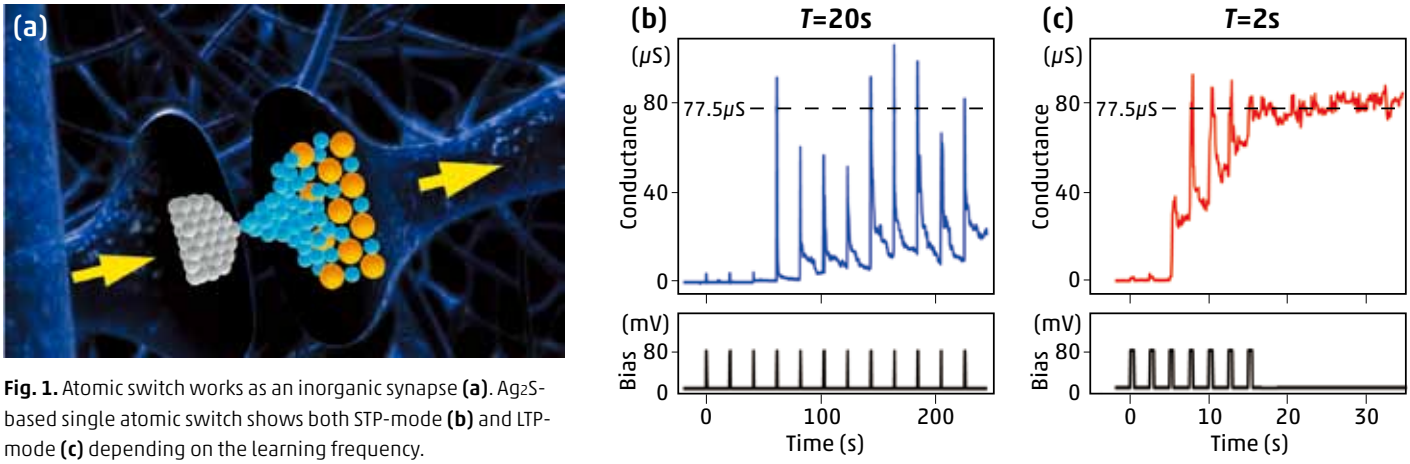


Fig. 1. Atomic switch works as an inorganic synapse **(a)**. Ag_2S-based single atomic switch shows both STP-mode **(b)** and LTP-mode **(c)** depending on the learning frequency.

04 Atomic Switch Networks: A new approach to neuromorphic computation

Representative researchers: **J. Gimzewski, A. Stieg, M. Aono**

Biological inspiration: Atomic Switch Networks use nanoscale materials to mimic cognition, learning

Atomic Switch Networks (ASN) are a unique class of biologically inspired computing architectures designed to produce a complex, dynamical system through the collective interactions of functional nanoscale materials. These self-organized devices retain the properties of their of component atomic switch elements, generate a class of emergent behaviors known to underlie biological cognition, and have demonstrated a capacity to perform computational tasks without a need for pre-programming.

Exceptional differences between the information processing capabilities of the brain and CMOS technology have led to a reexamination of artificial intelligence, neural networks, and neuromorphic systems. CMOS architectures consume orders of magnitude more energy than biological systems and are poorly suited for processing distributed data sets in real-time. By combining atomic switch technology with the advantages of self-organization, ASN devices comprise massively interconnected networks at a density of ~10^8 synthetic synapses/cm^2. Similar to neuronal networks, interactions between atomic switches produce emergent patterns of distributed activity[1]. Neural systems and ASNs alike can be classified as operating in a critical state[2], at the border of order and chaos, where correlations and mutual information are maximized amongst all elements in the network. Utilizing ASN dynamics has been facilitated by reservoir computing (RC), a biologically inspired computational model[3] capable of performing tasks that require the processing of multiple inputs such as pattern recognition, autonomous control, and analysis of real-time data from financial markets or neural activity. Of particular interest are the speed, density, and scalability of the ASN, which promise to overcome major hurdles in the RC paradigm. Experimental results have shown the ASN to be capable of performing various benchmark machine-learning tasks including the parity test and T-maze. The striking similarities of ASNs to biological control systems represent a paradigm shift from current CMOS-based technologies with revolutionary implications for real-time neuromorphic computation, making this an optimal time to explore the interface of complexity, neuroscience and engineering through nanoarchitectonics.

Main papers

1) A.V. Avizienis, H.O. Sillin, C. Martin-Olmos, H-.H. Shieh, M. Aono, J.K. Gimzewski, "Neuromorphic atomic switch networks". *PLoS ONE* **7** (2012) e42772.

2) A. Z. Stieg, A. V. Avizienis, H. O. Sillin, C. Martin-Olmos, M. Aono, J. K. Gimzewski, "Emergent criticality in complex Turing B-type atomic switch networks". *Advanced Materials* **24** (2012) 286.

3) H.O. Sillin, H.H. Shieh, R. Aguilera, A.V. Avizienis, M. Aono, A.Z. Stieg, J.K.Gimzewski, "A theoretical and experimental study of neuromorphic atomic switch networks for reservoir computing". *Nanotechnology* **24** (2013) 384004

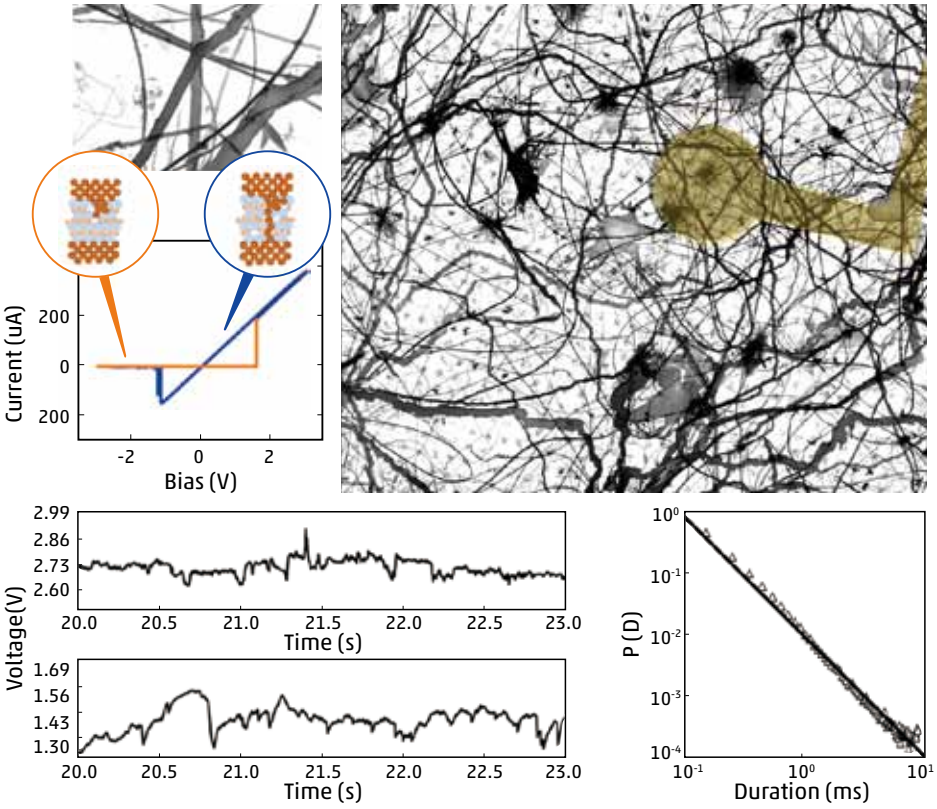


Fig. 1. A self-assembled network of Ag nanowires coated in Ag_2S (top right) with underlying Pt measurement electrodes (yellow) generates atomic switches at nanowire intersections (top left). ASN devices display pinched hysteresis I-V behavior (middle left) alongside complex interactions of many switches in the network (bottom left). Distributed activity across the entire device indicates critical-state dynamics (bottom right).

05 Electrical wiring of single molecules via conductive molecular chains

Representative researchers: **Y. Okawa, M. Aono**

Tiny circuitry: Linking single organic molecules and investigating conductivity

Though single-molecule electronics has been widely investigated for a long time, the fabrication of practical single-molecule circuits remains challenging because of the lack of viable methods for wiring each molecule. To solve this problem, we have developed a novel method for single molecular wiring. Using a nanoscale-controlled chain polymerization on a molecular layer, we have succeeded in connecting single conductive polymer chains to single functional molecules via covalent bonds. We are investigating the electrical transport properties of the fabricated single molecule devices. These studies will be an important step in advancing the development of single-molecule electronic circuitry.

We found before that stimulation with the tip of scanning tunneling microscope (STM) on a molecular layer of diacetylene compound could initiate chain polymerization of diacetylene molecules, where unsaturated diacetylene moieties add on to a growing polymer chain one after another in something like a "domino effect". As a result, we could fabricate a single conductive polydiacetylene chain at designated positions. Based on these previous studies, we have developed a novel method for connecting single conductive polymer chains to single organic molecules. Figure 1(a) shows a schematic illustration of the wiring procedure, which we call "chemical soldering". First, the relevant functional molecules are placed on a self-assembled monolayer of a diacetylene compound. The probe tip of the STM is then positioned on the molecular row of the diacetylene compound to which the functional molecule is adsorbed, and a conductive polydiacetylene chain (shown as yellow lines in Fig. 1) is fabricated by initiating chain polymerization by stimulation with the tip. Because the front edge of chain polymerization necessarily has a reactive chemical species, when the chain propagation encounters an adsorbed single functional molecule, a covalent bond is formed spontaneously. We have demonstrated that two polydiacetylene chains are connected to a single phthalocyanine molecule (Fig. 1(b)). The fabricated phthalocyanine-polydiacetylene system is expected to act as a resonant tunneling diode. First principles theoretical calculations, together with the detailed analysis of STM images, have been used to investigate the structures and electronic properties of the connection. The obtained structure is a single functional molecule connected to linear conductive polymers that can be several hundred nanometers long, and is ideal for investigating the electrical transport properties of organic connections and organic conductors.

Main papers

1) "Chemical wiring and soldering toward all-molecule electronic circuitry", Y. Okawa, S. K. Mandal, C. Hu, Y. Tateyama, S. Goedecker, S. Tsukamoto, T. Hasegawa, J. K. Gimzewski, M. Aono, *J. Am. Chem. Soc.* **133** (2011) 8227.

2) "Controlled chain polymerisation and chemical soldering for single-molecule electronics", Y. Okawa, M. Akai-Kasaya, Y. Kuwahara, S. K. Mandal, M. Aono, *Nanoscale* **4** (2012) 3013.

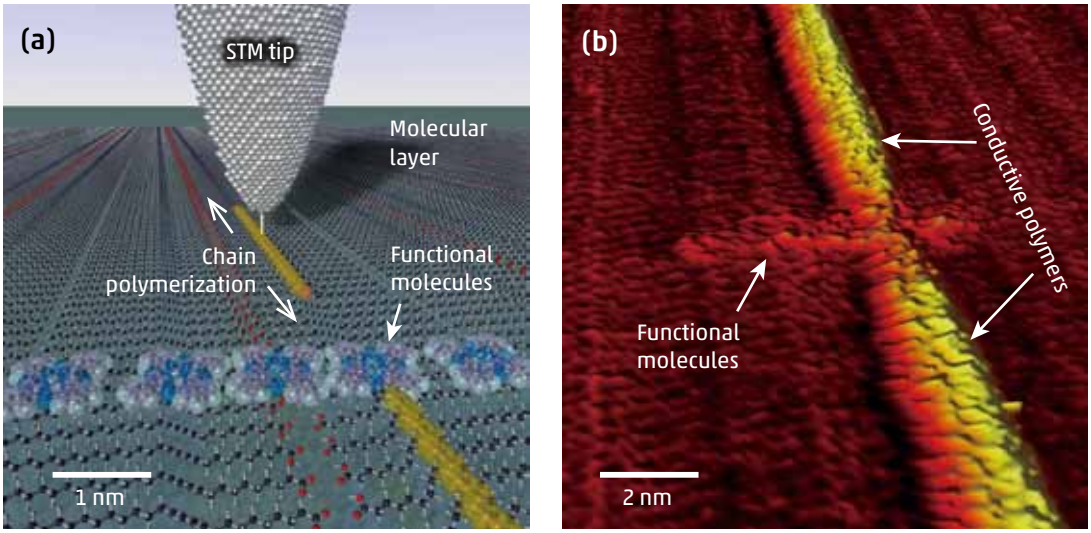


Fig. 1. Schematic illustration **(a)** and STM image **(b)** of chemical soldering. Chain polymerization is initiated with the STM tip. Two conductive polymer chains are connected to a single functional molecule (phthalocyanine).

06 Controlling bound and unbound states of molecules (C_{60}) reversibly at designated sites

Representative researchers: **T. Nakayama, M. Aono**

Molecular bit: Single molecule chemical reaction opens way to ultra-dense data storage

Ultrahigh-density data storage has been considered to be one of the important outcomes by utilizing single-molecule manipulation with a scanning tunneling microscope (STM). However, there has been a crucial problem for many years; how to achieve reversible and repeatable control of a molecular bit to represent 0 and 1. We solved this long-standing problem by reversibly controlling bound and unbound states of C_{60} molecules at room temperature, and demonstrated actual bit operations at a bit density of 190 Tbits/in^2.

We used a thin film of fullerene C_{60} molecules and controlled single-molecule-level chemical reaction between C_{60} molecules in the film using an STM tip. We found that negative and positive ionization of a designated C_{60} molecule can selectively trigger polymerization and depolymerization reactions of a designated C_{60} molecule, respectively, with an adjacent molecule in the film. The mechanism of this STM-induced chemical reaction was experimentally and theoretically studied. When the film of C_{60} molecules is negatively biased against an STM tip, electron donation to C_{60} molecules occurs under the tip and the lowest unoccupied molecular orbital (LUMO) of C_{60}, the bounding state between C_{60} molecules, is partially occupied. Further electronic excitation by tunneling electrons fulfills the bound state with two electrons, stabilizing the bound C_{60} molecule. When using opposite biases, the bound C_{60} molecules are positively ionized by extraction of electron. The destabilized bound state finally dissolves with the help of electronic excitation by tunneling electrons. Because electronic excitation by STM is in a very confined space, only a single C_{60} molecule underneath the STM tip can be controlled. Bound and unbound states of C_{60} molecules are easily recognized by the appearance and disappearance of depression of the film, and we demonstrated ultradense data storage by controlling the chemical reactions at a single-molecule precision as shown in Fig.1.

Main Papers

1) "Molecular-scale control of unbound and bound C_{60} for topochemical ultradense data storage in an ultrathin C_{60} film", M. Nakaya, S. Tsukamoto, Y. Kuwahara, M. Aono, T. Nakayama, *Adv. Mater.* **22** (2010) 1622.

2) "Molecular-scale size tuning of covalently bound assembly of C_{60} molecules", M. Nakaya, M. Aono, T. Nakayama, *ACS Nano* **5** (2011) 7830.

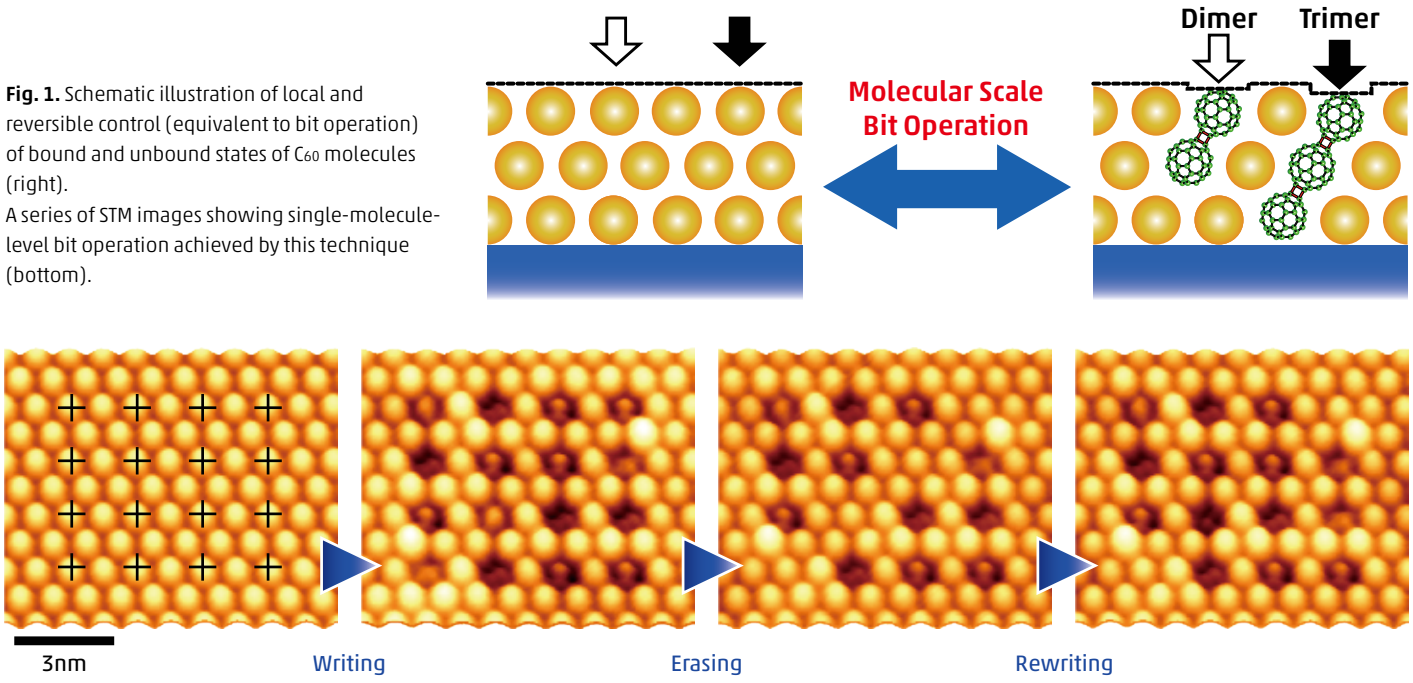
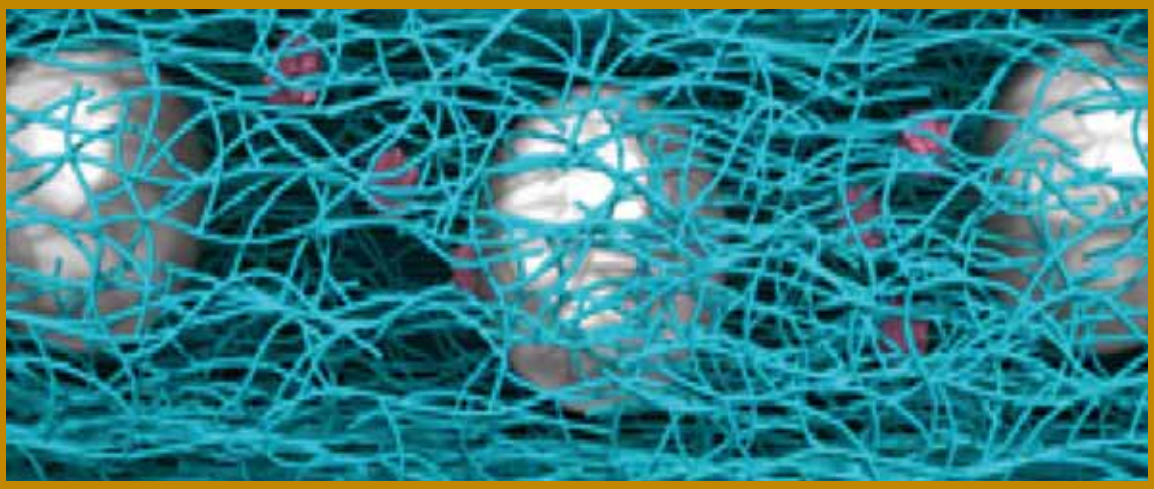
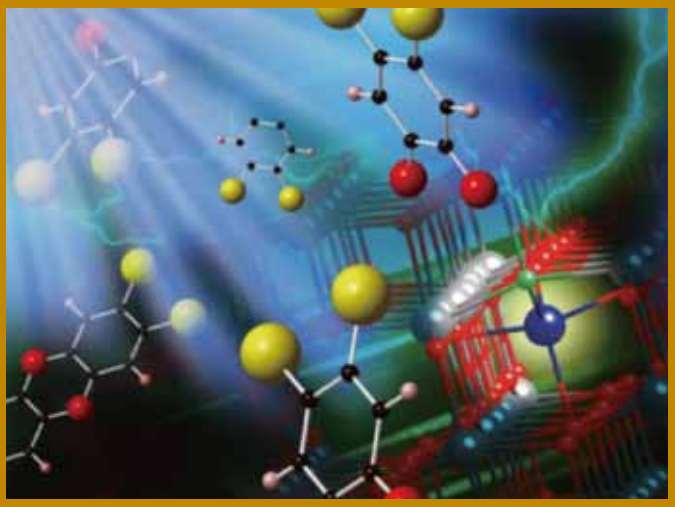
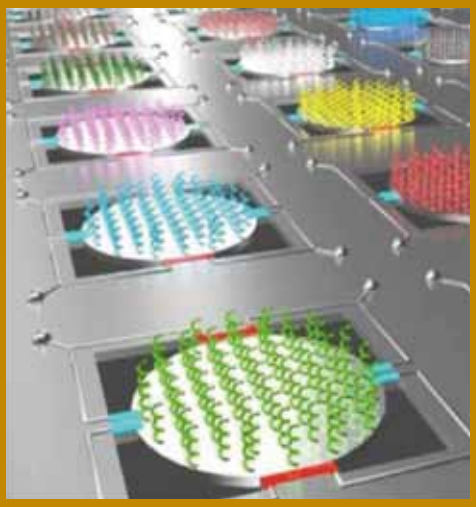
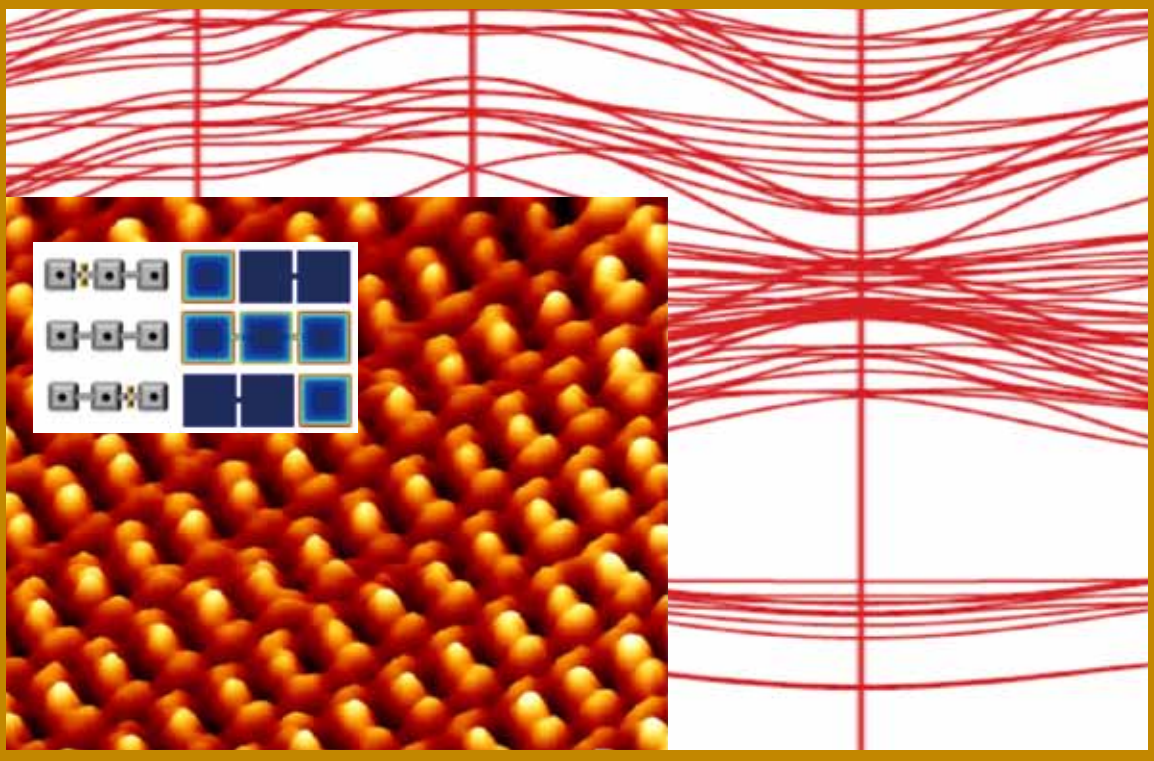


Fig. 1. Schematic illustration of local and reversible control (equivalent to bit operation) of bound and unbound states of C_{60} molecules (right).
A series of STM images showing single-molecule-level bit operation achieved by this technique (bottom).









Fusion of Interdisciplinary Research Fields

Nanoarchitectonics-inspired Nano-life Science

Nano-life Science-inspired Nanoarchitectonics

Theory-Experiment 'Cross-linkage' for Exploring Novel Nanoscale Materials and Systems

07 Nanoarchitectonic smart nanofibers for cancer therapy

Representative researchers: **M. Ebara, T. Aoyagi**

Fighting cancer: Nanofiber mesh supplies heat and chemotherapy to improve cancer treatment

We have developed a smart anticancer nanofiber capable of simultaneously performing thermotherapy and chemotherapy for treating malignant tumors. By tailoring the nano-architectures of the polymer networks in the fiber, we demonstrated simultaneous heat generation and drug release in response to alternating magnetic field (AMF). Only 5–10 min application of AMF can successfully induce apoptosis in cancer cells in both in vitro and in vivo studies.

Squamous cell carcinoma is an epithelial malignant tumor found in mucous membranes lined by stratified squamous epithelium and in the skin. At present, the main therapeutic methods are surgery, radiation therapy and chemotherapy, according to the stages of the cancer. In recent years, thermotherapy (or hyperthermia), which takes advantage of the fact that cancer cells are more sensitive to heat than normal cells, has attracted great attention. Since thermotherapy is also effective for enhancing drug efficacy and relieving pain, high expectations are placed on its combined use with chemotherapy and other types of therapy. In this research, we developed a mesh material which can be applied directly to the affected part, and which is capable of simultaneously performing thermotherapy and chemotherapy for treating epithelial malignant tumors. The nanofiber is composed of a chemically-crosslinkable temperature-responsive polymer with an anticancer drug and magnetic nanoparticles (MNPs), which serve as a trigger of drug release and a source of heat, respectively. By tailoring the nanoarchitectures of polymer networks in the fiber, the nanofiber mesh shows switchable changes in the swelling ratio in response to alternating 'on-off ' switches of AMF because the self-generated heat from the incorporated MNPs induces the deswelling of polymer networks in the nanofiber. Correspondingly, the 'on-off' release of drug from the nanofibers is observed in response to AMF. Both in vitro and in vivo studies show that the majority of tumor cells died in only 5–10 min application of AMF by the double effects of heat and drug. Taken together these advantages on both the nanoscopic and macroscopic scale of nanofibers demonstrate that the dynamically and reversibly tunable structures have the potential to be utilized as a manipulative hyperthermia material as well as a switchable drug release platform by simply switching an AMF 'on' and 'off '. We believe that the development of a manipulative material is very likely to lead not only to improving the survival rate of cancer patients but also to providing minimally invasive treatment methods in combination with endoscopic surgery.

Main papers

1) "A smart nanofiber web that captures and release cells", Y.-J. Kim, M. Ebara, T. Aoyagi, *Angew. Chem. Intl. Ed*. **51** (2012) 10537.
2) "A Smart Hyperthermia Nanofiber with Switchable Drug Release for Inducing Cancer Apoptosis", Y.-J. Kim, M. Ebara, T. Aoyagi, *Adv. Func. Mater*. **23** (2013) 5753.

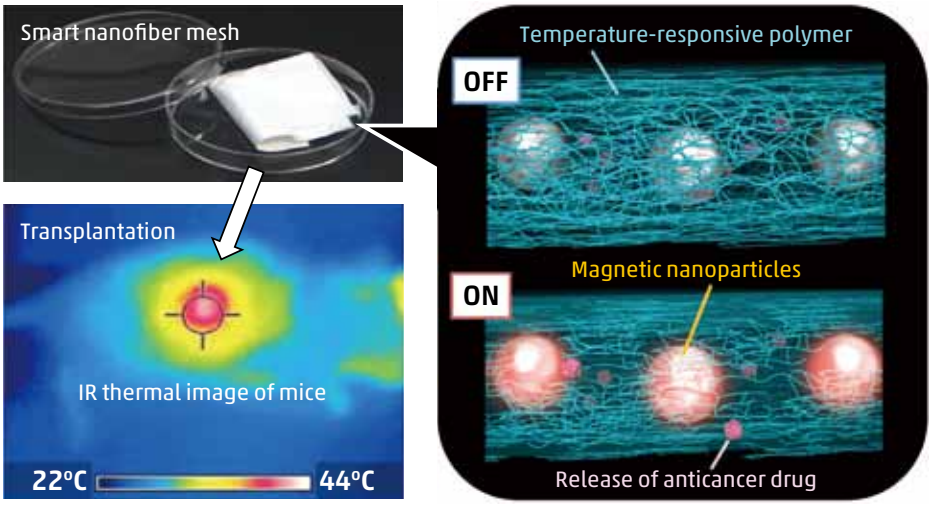


Fig. 1. Infrared (IR) thermal image of mice after the transplantation of smart anticancer nanofiber mesh which is composed of a chemically-crosslinkable temperature-responsive polymer with an anticancer drug and magnetic nanoparticles.

08 Novel nanoarchitectonic therapeutics – Complete recovery from Alzheimer's disease

Representative researcher: **Y. Nagasaki**

Conquering brain disease: Novel polymer cures cognition in Alzheimer model mice

Surprisingly, reactive oxygen species (ROS) have been known to affect more than 90% of diseases. Conventional drugs are problematic because of limited efficiencies along with severe adverse side effects. Guided by a nanoarchitectonic strategy, we have developed novel anti-oxidative polymer therapeutics which achieved complete recovery of cognition in Alzheimer model mice.

With advancing age, the production of ROS increases remarkably and endogenous antioxidants fail to scavenge ROS completely. Such excess of ROS continuously amplifies inflammation, thereby increasing the risk of potentially life-threatening disorders. Although many promising antioxidants have showed efficiency, the results of clinical trials have been negative because of drug metabolism, rapid elimination or side effects on the body. We have developed "orally administered redox polymer therapeutics" for cognitive deficit disorders. This polymer possesses nitroxide radicals for ROS scavenging in the hydrophobic segment via covalent linkage (PEG-b-PMNT). PEG-b-PMNT forms polymeric micelle under physiological conditions, which confines nitroxide radicals in its core and is 40 nm in diameter (RNP). Because RNP disintegrates under acidic conditions in the stomach, we hypothesized PEG-b-PMNT is absorbed into the bloodstream via mesentery. Since polycationic proteins and macromolecules are reported to not only bind to the endothelial cell surface but also penetrate the BBB via adsorptive transcytosis, PEG-b-PMNT may pass through the BBB. Because nitroxide radicals are covalently linked to block copolymers, they may be internalized together with polymer in the brain, which is in sharp contrast to the physically drug-loaded nanoparticle delivery system. Because the molecular weight of PEG-b-PMNT is ca. 8 – 15KDa, it is hard to internalize into healthy cells. This prevents adverse effects unlike conventional low molecular weight antioxidants, which damage normal redox reaction such as electron transport chains in cells. As shown in Fig.1(b), the cognition level of senescence accelerated mice (SAMP8) was completely restored after oral administration of our redox polymer based nanoparticle (RNP).

Main papers

1) "An orally administered redox nanoparticle that accumulates in the colonic mucosa and reduces colitis in mice", L. B. Vong, T. Tomita, T. Yoshitomi, H. Matsui, Y. Nagasaki, *Gastroenterology* **143** (2012) 1027.

2) "Direct observation of adsorption-induced inactivation of antibody fragments surrounded by mixed-PEG layer on a gold surface", Y. Keitaro, N. Motohiko, S. Hiroaki, N. Yukio, *J. Am. Chem. Soc.* **132** (2012) 7982.

3) "A smart nanoprobe based on fluorescence-quenching PEGylated nanogel containing gold nanoparticles for monitoring the cancer response to therapy, O. Motoi, T. Atsushi, N. Takahito, N. Yukio, *Advanced Functional Materials* **19** (2009) 827.

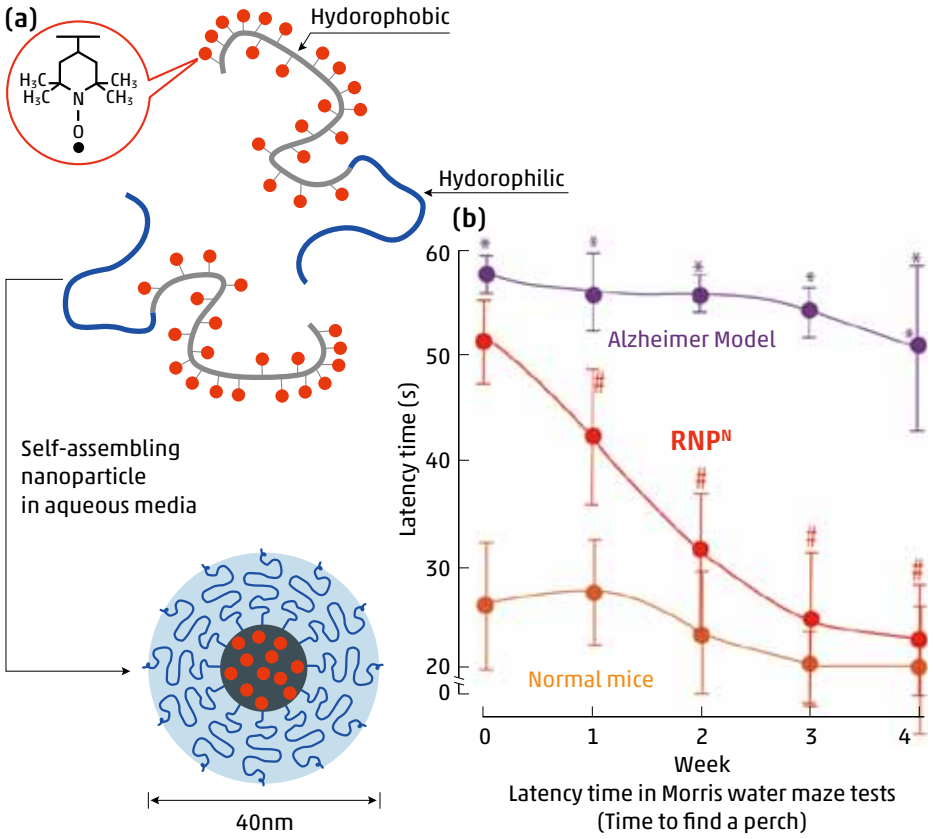


Fig. 1. (a) Design of Novel Nanoarchitectonic therapeutics. **(b)** Therapeutic effect of RNP on cognitive dysfunction. RNP improved the latency period of SAMP8 mice in the Morris water-maze test (Latency time was determined by the time to find a rest place in water pool).

09 Ultrasensitive and ultraparallel molecular sensing for use in artificial noses and other applications

Representative researchers: **G. Yoshikawa, M. Aono**

Super sensor: Unique molecular sensor offers abundant health, security and environmental applications

We have developed a novel molecular sensor, which researchers worldwide have been trying to realize these last 20 years. We named the new sensor "Membrane-type Surface stress Sensor (MSS)". Significant improvements in sensitivity as well as in all the practical aspects pave the way for implementing nanoarchitectonic technologies in real-life applications.

The MSS was developed through comprehensive optimization of the technologies of various relevant fields--materials science, mechanics, crystallography, and electronics--investigated together with Dr. Heinrich Rohrer (Nobel Prize Winner in Physics 1986) and the MEMS team in SAMLAB, EPFL, Switzerland. The unique structure of MSS, shown in Fig. 1(a), has led to more than 100 times higher sensitivity in addition to the better performance in all practical aspects, such as higher reproducibility, higher mechanical and electrical stability, simpler operation, smaller size, and lower cost. As shown in Fig. 1(b), an array of MSS can be integrated in a rather small footprint. "Non-invasive breath analysis" is one of the potential applications of MSS. Figure 1(c) shows that an array of MSS coated with various receptor polymers could distinguish the breath of cancer patients from that of healthy people in a double blind trial. These results encourage us to develop a new type of a diagnostic module which can be integrated in mobile devices, such as a cell phone, to help maintain a healthy physical condition automatically. The compatibility with double-side coating enables MSS to be applied to most standard assays in medical and biological fields. Because MSS can detect almost any kind of molecules ranging from gaseous to biological species under various conditions including opaque liquids such as blood, MSS is expected to contribute to global challenges in medicine, security, and environmental research. The development of MSS won the Tsukuba Encouragement Prize.

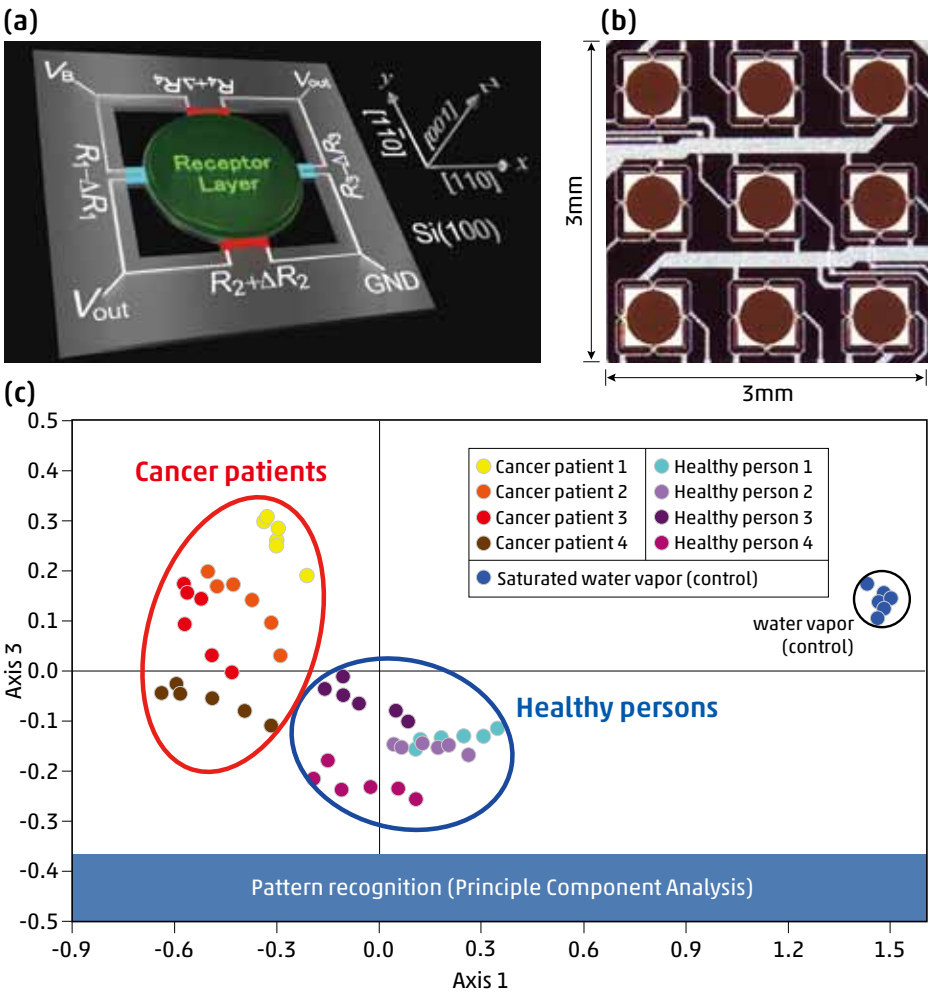


Fig. 1. Ultrasensitive / ultraparallel MSS works as an artificial diagnostic nose. **(a)** Schematic image of MSS structure. **(b)** Photo image of an array of MSS fabricated in collaboration with SAMLAB, EPFL. **(c)** Experimental results of breath analysis of cancer patients and healthy persons.

Main papers

1) "Nanomechanical membrane-type surface stress sensor", G. Yoshikawa, T. Akiyama, S. Gautsch, P. Vettiger, H. Rohrer, *Nano Letters* **11** (2011) 1044.
2) "Double-side-coated nanomechanical membrane-type surface stress sensor (MSS) for one-chip- one-channel setup", G. Yoshikawa, F. Loizeau, C. J. Lee, T. Akiyama, K. Shiba, S. Gautsch, T. Nakayama, P. Vettiger, N. F. de Rooij, M. Aono, *Langmuir* **29** (2013) 7551.
3) F. Loizeau, H. P. Lang, T. Akiyama, S. Gautsch, P. Vettiger, A. Tonin, G. Yoshikawa, C. Gerber, N. de Rooij, *Proceedings IEEE MEMS* **26** (2013) 621.

10 Progress in high-efficiency artificial photosynthesis

Representative researcher: **J. Ye**

Environmental progress: Artificial photosynthesis advancement heralds solution to global warming, energy shortage

We have been conducting a series of pioneering works for challenging a high-efficiency artificial photosynthesis, which offers potential solution for global warming and energy shortage issues. A new material Ag_3PO_4 with the world's highest quantum efficiency (approaching that of natural photosynthesis) in photocatalytic water oxidation has been developed by an unique material-designing guideline. Sophisticated control of surface/interface structure has enabled efficienct light harvesting, charge seperation, and gas diffusion/conversion, making a big step towards realization of a high-efficiency artificial photosynthesis.

As a nano-life science-inspired nanoarchi-tectonics, here we demonstrate an unique strategy for constructing a promising 3D artificial photosynthetic system (APS) for efficient CO_2 photoreduction into hydrocarbon fuels. Natural leaf, an assembly of 3D elaborated architectures with high porosity, high connectivity and high surface areas, is a synergy of complex architectures and functional components to produce an amazing bio-machinery for photosynthesis (Fig.1). Mimicking the structural and functional elements in the natural photosynthesis, which were created in the course of evolution, can be considered as one of the most effective approaches to achieve an efficient artificial photosynthetic system.

In this work, by using leaves of cherry tree as the template, we have successfully fabricated perovskite titanates with a modified sol-gel method. After acid treatment and calcination at 600°C, organics could be removed completely, leaving crystalline perovskite titanates. The obtained material preserves the morphological features of leaf at levels ranging from nano- micro-macro scale (Fig.1).

Artificial photosynthesis is performed using H_2O and CO_2 as the reactants under UV-Vis light irradiation. It was found that leaf-architectured $SrTiO_3$ exhibits about a 3.5–4 fold improvement in activities than the referenced $SrTiO_3$ synthesized without templates. A further mechanism study revealed that the enhanced conversion efficiency can be attributed to not only the increased surface area, but also the three dimensionally inter- connected tunnel structure of leaf-template which is apparently favorable for efficient mass flow such as CO_2 adsorption/diffusion/conversion as well as light harvesting. This study is the first example utilizing biological systems as "architecture-directing agents" for APS towards CO_2 photoreduction, which hints at a more general principle for APS architectures with a great variety of optimized biological geometries. This research would have great significance for the potential realization of global carbon neutral cycle.

Main papers

1) "Leaf-architectured 3D hierarchical artificial photosynthetic system of perovskite titanates towards CO_2 photoreduction into hydrocarbon fuels", H. Zhou, J. Guo, P. Li, Tongxiang Fan, Di Zhang, J. Ye, *Scientific Reports* **3** (2013) 1667.

2) "An orthophosphate semiconductor with photooxidation properties under visible-light irradiation", Z. Yi, J. Ye, N. Kikugawa, T. Kako, S. Ouyang, H. Stuart-Williams, H. Yang, J. Cao, W. Luo, Z. Li, Y. Liu, R. L. Withers, *Nature Mater.* **9** (2010) 559.

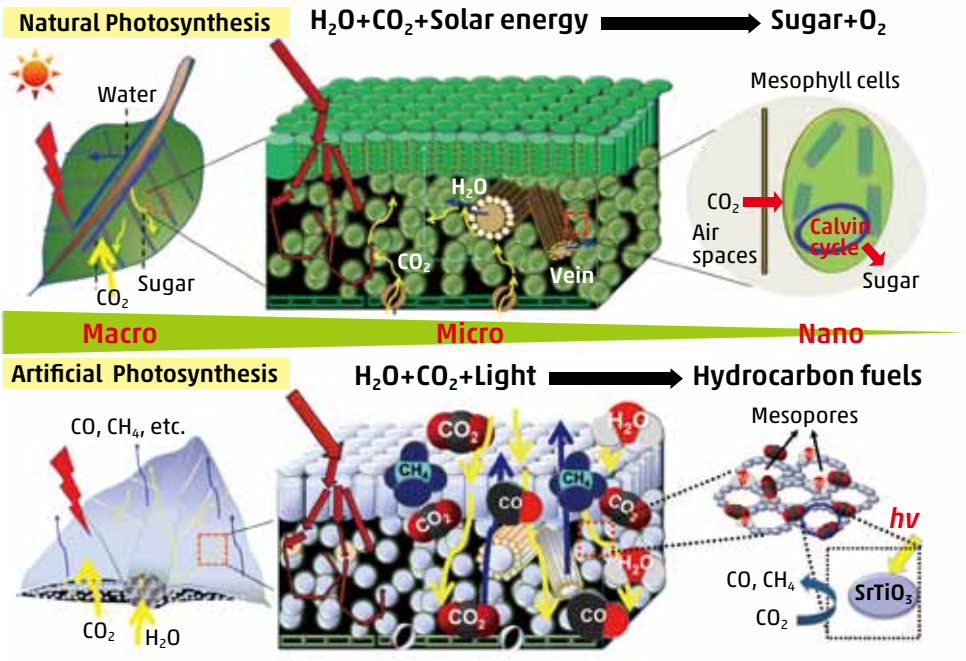


Fig. 1. Schematic illustration and comparison of the structure and key processes in natural photosynthetic system (top) and artificial photosynthetic system (bottom).

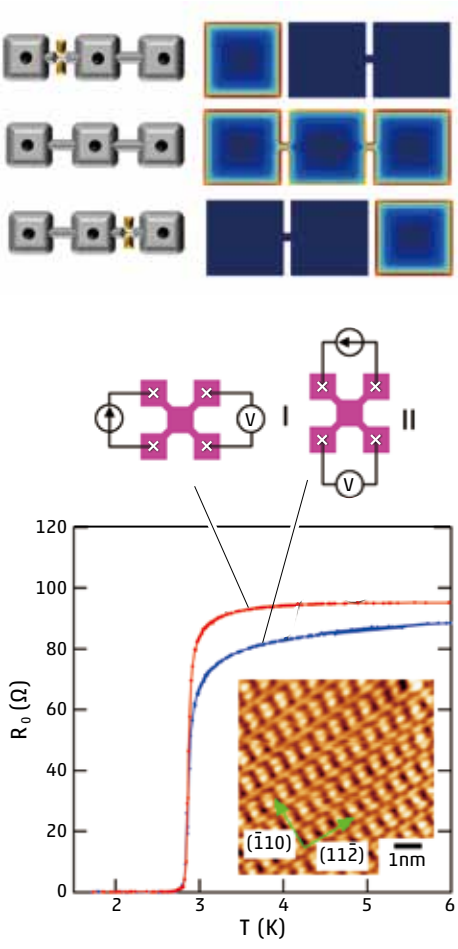
11 Topological matter nanoarchitectonics for novel quantum devices

Representative researchers: **X. Hu, T. Uchihashi**

Exploring Novel Quantal Property for Revolutionary Functionality

Because the uncertainty of quantum mechanics becomes prominent, functionalities of nano devices are hard to be realized upon design similar to those in macroscopic and microscopic scales. In order to develop new design principles for advanced quantum devices, we exploit topology of electron systems, which bridges bulk to surface and nano to macro as a quantum holography principle. A brand-new approach coined topological matter nanoarchitectonics is emerging.

Topological systems are commonly accompanied by unique surface states, such as zero-energy Majorana fermion (MF) in a topological superconductor (TS), and quantized current in a topological insulator (TI), which can be used for developing advanced quantum functionalities.



We have proposed a system of nano TSs with their connections controlled by pinch-off voltages, where one vortex is trapped at the center at individual TSs (Fig. 1). Existing only at perimeters which include odd-number of vortices, MFs can be generated and transported efficiently and stably by switching on and off gate voltages in between TSs. The collapsing of MF wave function to the right TS upon pinching off the link between the middle and right TSs displayed in Fig. 1 is a topological property unique to MFs, which cannot be achieved with electrons and photons. Marvelously non-Abelian quantum statistics can be realized by exchanging positions of MFs. Being half pieces of electrons, MFs can be used to compose qubits, which are robust to local noises since MFs are charge neutral and placed separately in space.

In order to realize TS state experimentally, we are working on an atomically thin superconductor on semiconductor surface with the Rashba effect and self-assembling of magnetic molecules. We demonstrate successfully the surface superconductivity by direct transport measurements (Fig. 1) for the first time in the world. For the Si(111)-(√7×√3)-In surface, we have observed onset of the zero-resistance state below Tc ~3K. *I-V* characteristics are found to exhibit switching between superconducting and normal states with well-defined critical currents. The large critical current density found there means that this surface monolayer material can be used for practical superconducting devices. The temperature dependence of the critical current density indicates that the surface atomic steps play the role of Josephson junctions, which was independently confirmed by direct observation of vortices in a scanning tunneling microscope experiment. We have successfully demonstrated self-assembly of magnetic molecules on this surface superconductor, and observed strong exchange interaction between the magnetic molecule and the superconducting layer, which is indispensible for the realization of TS state and MFs.

We have also designed a novel TI system where the edge state carries zero-resistance current even above room temperature. The current is spin polarized and reversible by electric field, ideal for spintronics.

Fig. 1. Device of Majorana fermions (MFs). Connections among superconductors are controlled by pinch- off voltages at the constrictions, which drives MFs (top). Temperature dependence of zero bias resistance of the Si(111)-(√7×√3)-In reconstruction. The inset shows the STM image of the sample surface (bottom).

Main papers

1) "Manipulation of Majorana fermions by point-like gate voltage in the vortex state of a topological superconductor", Q.-F. Liang, Z. Wang, X. Hu, *Europhys. Lett.* **99** (2012) 50004 (Editor's choice).
2) "Macroscopic superconducting current through a silicon surface reconstruction with indium adatoms: Si(111)-(√7×√3)-In", T. Uchihashi, P. Mishra, M. Aono, T. Nakayama, *Phys. Rev. Lett.* **107** (2011) 207001(Editor's suggestion and featured in Physics).

12 Ultra-large-scale computation: Development and application of an advanced code

Representative researchers: **D. R. Bowler, T. Miyazaki, N. Fukata**

"CONQUEST": Advanced code enables massive simulations on range of systems

CONQUEST, a world-leading linear scaling density functional theory (DFT) code, has been developed to bridge the gap between experimental and theoretical investigations of organic and inorganic nanosystems . It is capable of modeling millions of atoms with DFT both accurately and robustly. We want to drive innovative experiments by the application of CONQUEST.

Modern electronic structure calculations are becoming an essential tool in research, both because of their accuracy and their predictive power. The most common approach is DFT, which is used in physics, chemistry, materials science, earth science, biochemistry and other fields. But standard implementations of DFT have a significant restriction on the size of the system that they can model, which comes from the scaling of the approach. The computational effort scales with the cube of the number of atoms, which imposes a practical limit of a few thousand atoms on DFT codes, even on the most powerful computers.

However, as electronic structure is local in space (known as "near-sightedness" by the Nobel Laureate Walter Kohn) the amount of effort required should scale only linearly with the number of atoms. With the freedom to apply *ab initio* methods to systems of tens of thousands to millions of atoms, our understanding of nano-science should be transformed.

To enable calculations on nano-scale systems which are the same size as those treated by experiment, we have developed the linear scaling DFT code, CONQUEST, which is leading the world in the size of systems that it can simulate, and in performance on high-performance computers. The code has demonstrated calculations on over two million atoms, and has shown robust, accurate calculations on many systems, including semiconductor nanostructures and biological molecules.

We show two examples of systems being investigated with CONQUEST in Fig.1. Ge self-assembles into characteristic three-dimensional structures when deposited onto Si(001), and we are studying how these structures form and grow. We are also working on an innovative experiment-theory project, exploring the location, mobility and properties of dopants in semiconductor nanowires, which may be used in nanoscale transistors, as shown in Fig.1 (bottom). We will understand the effect of dopant location on their properties, and learn how to control the location and motion of dopants during growth.

CONQUEST has been in beta testing for some time, and will be released freely to the scientific community in the near future. We are implementing important new functionality including molecular dynamics, time-dependent DFT and exact exchange, to further increase the accuracy and applicability of the method.

Main papers

1) "Calculation for millions of atoms with density functional theory: linear-scaling shows its potential", D. R. Bowler, T. Miyazaki, *J. Phys. Condens. Matter* **22** (2010) 074207.
2) "O(N) methods in electronic structure calculations", D. R. Bowler, T. Miyazaki, *Rep. Prog. Phys.* **75** (2012) 036503.

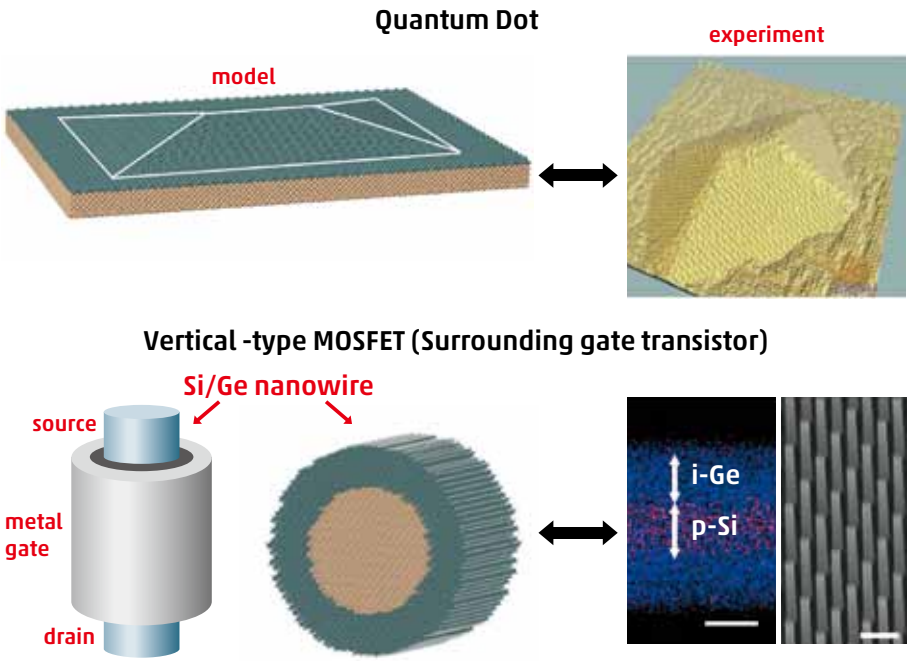
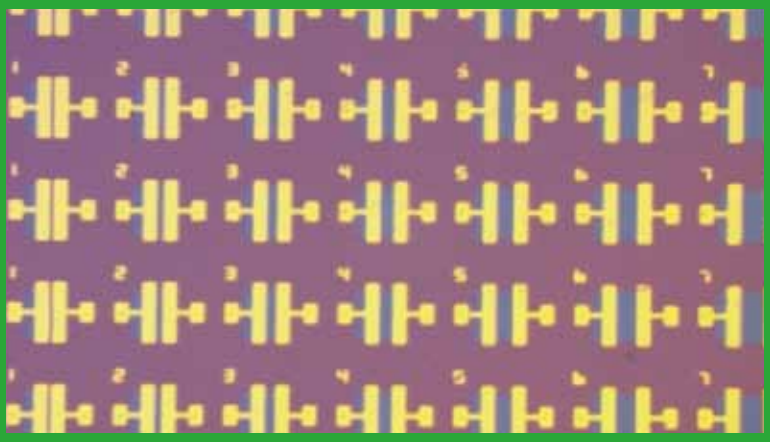
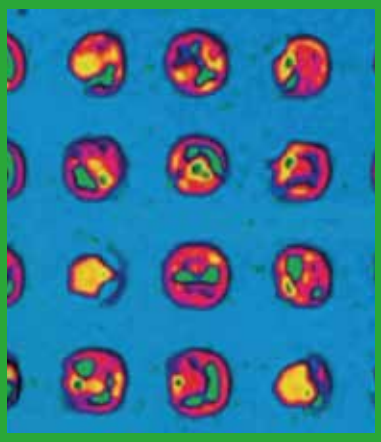
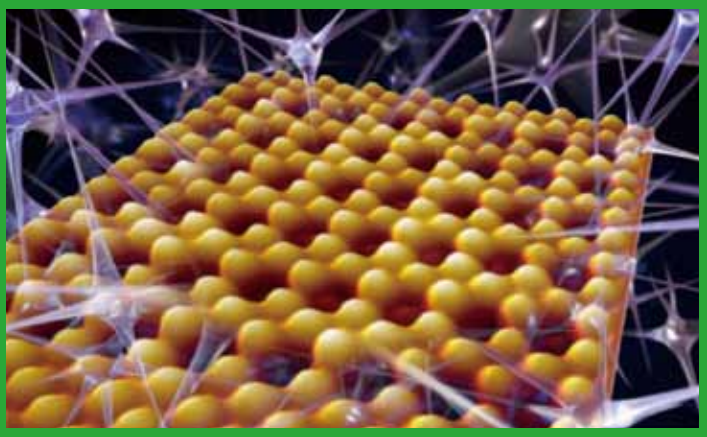
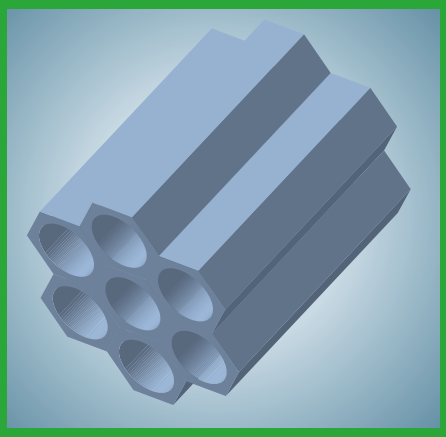


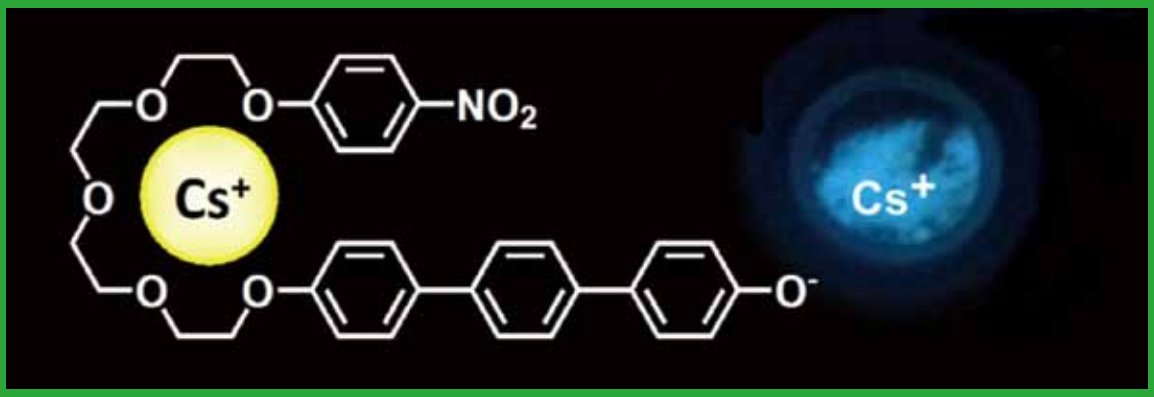
Fig. 1. Optimized structure of Ge nano-island on Si (001) substrate calculated using CONQUEST, and experimental structure (top). Atomic models of Si/Ge core-shell nanowire, along with TEM and SEM measurements and schematic of how nanowires can be used in transistors (bottom).







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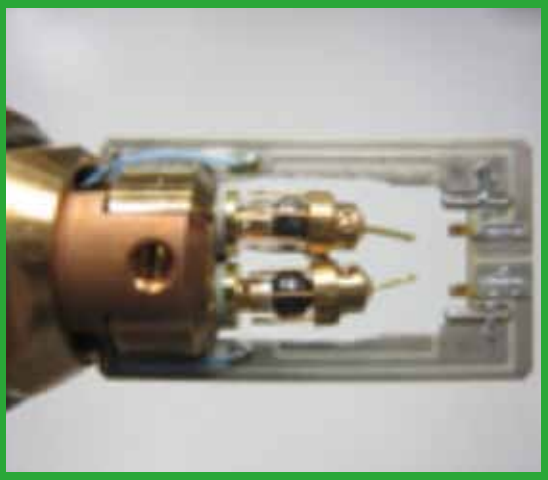
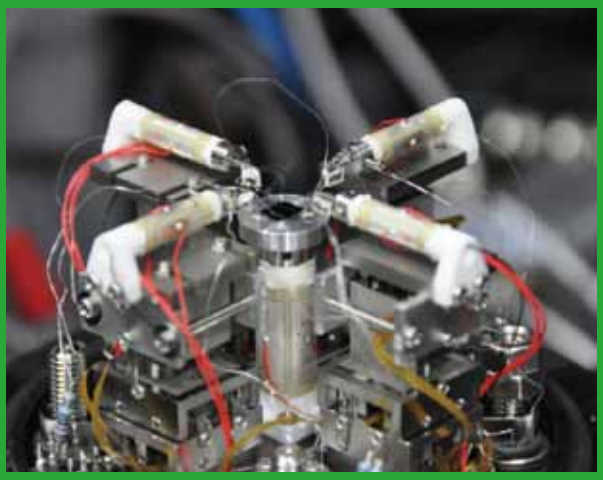




Other Remarkable Research Results

Innovative Nanoscale Devices and Systems

Innovative Nanoscale Characterization Methodologies

Nanoarchitectonics Related to Sustainable Energy and Environment

13 Mesoscopic superconductivity quantum phenomena in superconductor and normal-metal junctions

Representative researcher: **H. Takayanagi**

Studying junctions: Superconductor LED investigation uncovers new quantum phenomena

We have been working on mesoscopic superconductivity. In particular, we have treated superconductor (S) / normal-conductor (N) junctions, which has revealed various new quantum phenomena. As to N, we use normal metal, semiconductor two-dimensional electron gas, graphene, and quantum dot. In an S/N junction, electron Cooper pairs in S can penetrate into N (proximity effect). This effect results in many interesting quantum phenomena that can be applied in quantum information technology.

One of the most interesting superconducting mesoscopic devices is the superconductor light emitting diode (LED), Fig. 1. The superconductor LED is expected to be the key device in quantum information technology because of its promising giant oscillator strength due to the large coherence volume of the superconducting electron Cooper pairs together with the possibility of the *on-demand* generation of entangled photon pairs. The enhancement of the electroluminescence in the active layer accompanying the superconducting transition in the electrode (Nb in Fig. 1) was demonstrated, and theoretical understanding using second perturbation theory was established.

Superconductor LED in the strong light-confinement regime are characterized as a superconductor-based three- terminal device, and its transport properties are quantitatively investigated. In the gate-controlled region, we confirm the realization of a new-type Josephson field effect transistor (Fig. 2). In the current-injected region, the superconducting critical current of μA order in the Josephson junction is found to be modulated by the steady current injection of pA order. This ultrahigh sensitivity of the radiative recombination process can be explained by taking into account the fact that the energy relaxation of the absorbed phonons causes the conversion of Cooper-pairs to quasiparticles in the active layer. Using quasiparticle density and Cooper-pair density, we can discuss the carrier flows together with the non-equilibrium superconductivity in the active layer and the superconducting electrodes, which take place for compensating the conversion.

This work was done in collaboration with Hokkaido Univ., NTT and Hamamatsu Photonics.

Fig. 1 Quantum mechanically entangled photon pairs

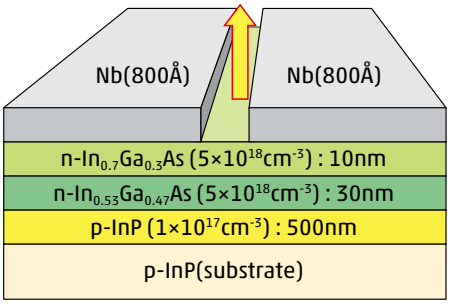
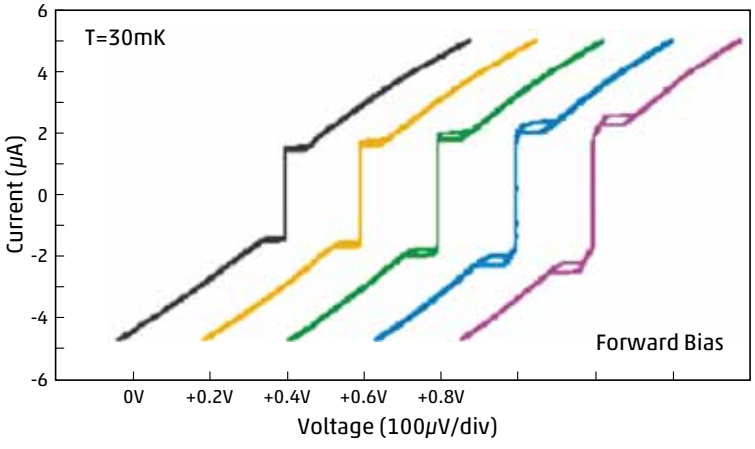


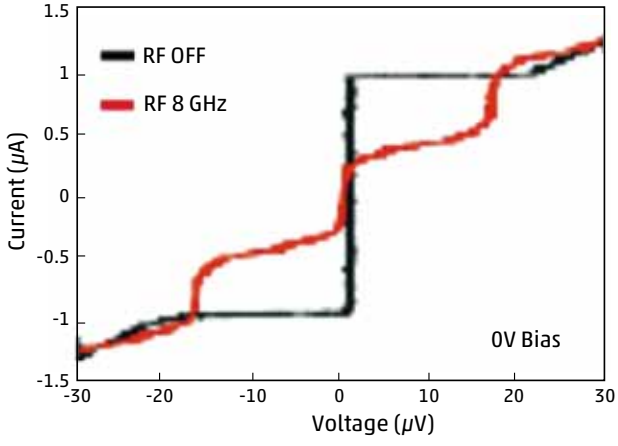
Fig. 1. Schematic cross-sectional view of the superconductor LED.
Fig. 2(a). Current-voltage characteristics of the Nb/n-InGaAs /Nb junction on the LED surface measured at 30 mK. A clear supercurrent is observed. **(b)** The data measured with 8 GHz microwave irradiation shows ac Josephson effect.

Main papers
1) "Nb/n-InGaAs/p-InP superconductor / semicon ductor-diode light emitting device" H. Sasakura, S. Kuramitsu, Y. Hayashi, K. Tanaka, T. Akazaki, E. Hanamura, R. Inoue, H. Takayanagi, Y. Asa no, H. Kumano, I. Suemune, *Phys. Rev. Lett.* **107** (2011) 157403.
2) "Luminescence of a Cooper Pair", Y. Asano, I. Suemune, H. Takayanagi, and E. Hanamura, *Phys. Rev. Lett.* **103** (2009) 187001.

Fig. 2 (a)



(b)



14 Silicon-doped metal oxide thin film transistor for flat panel application

Representative researchers: **K. Tsukagoshi, T. Nabatame**

Thin-film transistor: New material shows promise for energy-saving flat panel displays

For the next-generation amorphous metal-oxide thin film transistor (a-OxTFT), we found that the stability of the transistor properties strongly depends on the bond-dissociation energy of dopant element. Because the doped silicon in amorphous In_2O_3-based thin films is found to suppress the formation of unstable oxygen vacancies, silicon doped metal oxide TFTs (SiM-OxTFTs) behave as the stable high-performance a-OxTFT.

For the backplane transistor in a flat panel display, amorphous silicon or poly-silicon film is currently used for pixel switching. Because of serious leakage current in the off state of current TFTs, a new material TFT has been strongly desired to realize a low-power consumption flat panel. Amorphous metal oxide thin-film transistor (a-OxTFT) is a possible candidate as the post silicon TFTs. Although InGaZnO is one of the a-OxTFT candidates at the moment, the InGaZnO is widely known as an unstable film in actual production because of high-sensitivity to film-formation conditions.

We investigated a-OxTFTs doped with various doping species. In thermal cycle durability, we observed that the dopant in InOx film stabilized film properties. The electric properties of the a-OxTFT are determined by the bond-dissociation energy of the doped atom. By incorporating dopant with a higher bond-dissociation energy, the film becomes less sensitive to the oxygen partial pressure used during sputtering deposition and remains electrically stable to thermal treatment.

Here, we propose using a silicon doped OxTFT (SiM-OxTFT) as the high-performance a-OxTFT. This is because the bond dissociation energy of Si-O, 799 kJ/mol, is known as a very strong oxygen-metal bonding. The SiO_2 incorporated thin film transistors exhibiting reliable device characteristics after annealing at 250-300°C. Increasing the SiO_2 content of the sputtering target decreased the sensitivity of the subthreshold swing and turn-on voltage of the device to the sputtering conditions used to deposit the amorphous oxide, making them more stable against electrical and thermal stresses. Incorporating SiO_2 suppressed the de-population of donor-like traps and charge-carrier trapping at the semiconductor/insulator interface, which led to stable TFT operation. As the SiO_2 content increased, the activation energy in the current off region greatly increased and the density of the state at the band tail became small, resulting in stable transistor operations.

The results of the current study will facilitate mass production of highly stable amorphous InO-based thin-film transistors.

Main papers

1) "Thin-Film Transistors Fabricated with Low Temperature Process Based on Ga- and Zn-Free Amorphous Oxide ", S. Aikawa, P. Darmawan, K. Yanagisawa, T. Nabatame, Y. Abe, K. Tsukagoshi, *Appl. Phys.Lett.* **102** (2013) 102101.

2) "Doping Control in In-X-O Metal Oxide Semiconductors for Thin-Film Transistor Applications ", S. Aikawa, T. Nabatame, K. Tsukagoshi, *Appl.Phys.Lett.* **103** (2013) 172105.

3) "Stable amorphous In2O3-based thin-film transistors by incorporating SiO2 to suppress oxygen vacancies", N. Mitoma, S. Aikawa, X. Gao, T. Kizu, M. Shimizu, M.-F. Lin, T. Nabatame, K. Tsukagoshi, *Appl. Phys. Lett.* **104** (2014) 102103.

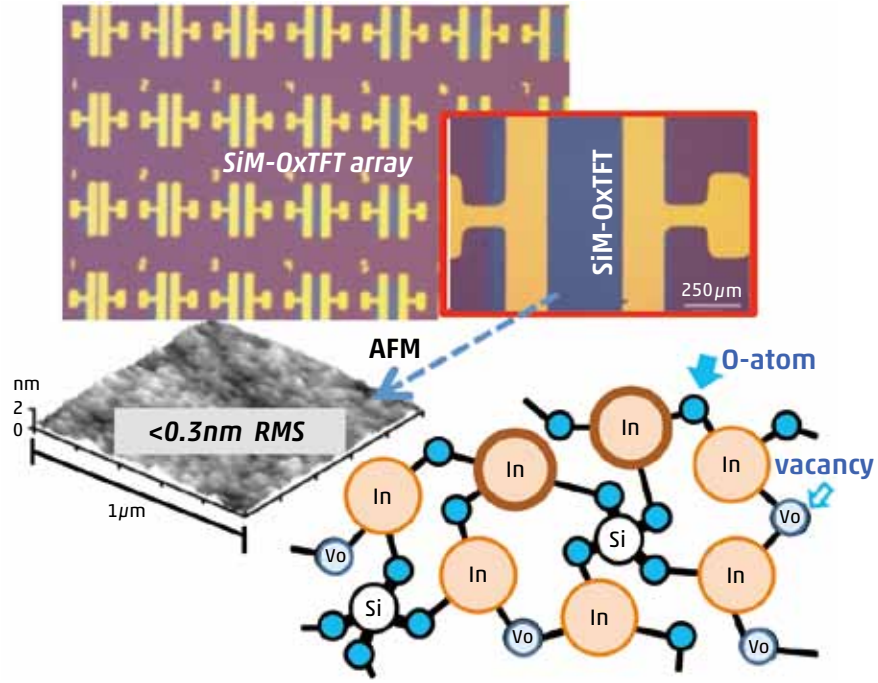


Fig. 1. Images of TFT composed of newly developed oxide film. Because of amorphous film, the surface is flat. Schematic of vacancy (V_o) suppression in a-InSiO film. White circles denote atoms with empty conduction bands, while gray circles denote atoms with partially occupied conduction bands.

15 Nanogenerators and self-powered nanosystems

Representative researcher: **Z. L. Wang**

Nanosystems: Study suggests potential for nanogenerators in environmental monitoring

A theoretical model for contact-mode triboelectric nanogenerators (TENGs) was constructed. Its real-time output characteristics and the relationship between the optimum resistance and TENG parameters were derived. The theory presented here is the first in-depth interpretation of the contact-mode TENG, which can serve as important guidance for rational design of the TENG structure in specific application.

The most important theoretical equation for representing the real-time power generation of a TENG is a relationship among three parameters: the voltage (V) between the two electrodes, the amount of transferred charge (Q) in between, and the separation distance (x) between the two triboelectric charged layers, which can be named the V–Q–x relationship. A theoretical model for contact-mode TENGs is presented in this work. The analytical model was built for both dielectric-to-dielectric and conductor-to-dielectric contact mode TENGs and their basic equations (V–Q–x relationship) were derived. Theoretical modeling of experimental results. From the basic equation, the real-time output characteristics were presented, showing three-working-region behavior when driving external resistance loads. The reason for this unique characteristic was mathematically interpreted. We further systematically studied the optimum resistance for the maximum instantaneous power and the influence of the TENG parameters, such as area size, average velocity, effective dielectric thickness, and the gap distance. Additionally, experiments were performed to verify these theoretical expected results. The theory presented here is the first in-depth interpretation and analysis of the contact-mode TENG's working principle, clearly showing its unique operation characteristics.

A control over humidity is necessary for improving quality of life and enhancing industrial processes. As a result, humidity sensors based on various working principles have been extensively adopted in environmental monitoring. Ethanol, as a representative organic liquid/gas, is related with biomedicine, brewing, and other chemical processes, and its accurate analysis both in blood and breathing is of importance to the monitoring and control drink and drive. We designed triboelectric nanogenerator (TENG) as self-powered active sensors for detection of humidity or alcohol content. These TENGs were made of polyamide 6, 6 (PA) film and PTFE film (PA TENG, PTFE TENG), respectively, which not only can detect liquid waters and ethanol, but also can probe gaseous water and ethanol. The response of the PTFE TENG for the ethanol gas is investigated and displayed in Fig. 1(a). Our study suggests that these TENG devices can be applied as self-powered active sensors for environmental monitoring and industrial manufacture with advantages of being low cost, simple fabrication, and good performance.

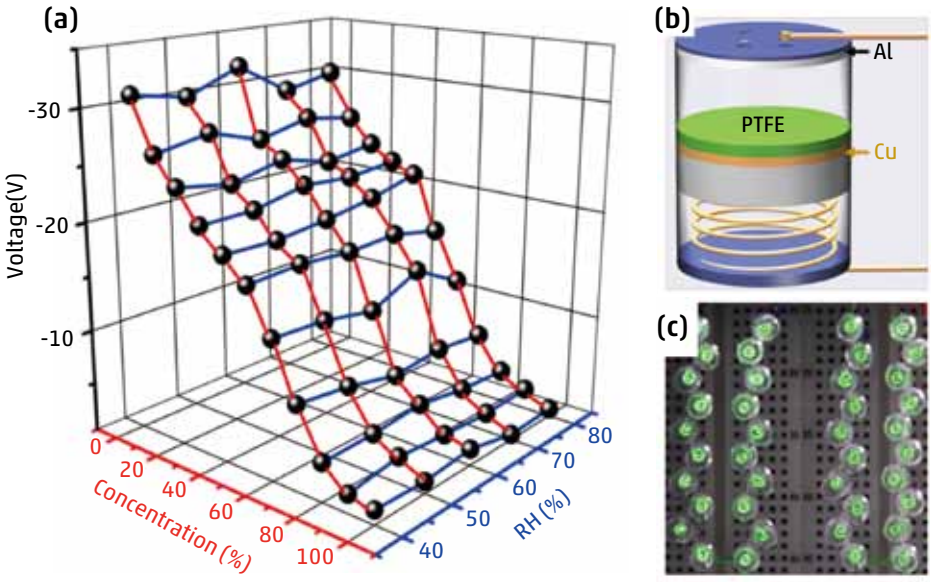


Fig. 1. (a) 3D graph of PTFE TENG sensor response to the changing external RH and ethanol concentration. **(b)** A schematic diagram of the fabricated device. **(c)** 40 LEDs lighted up by the TENG device before dripping ethanol.

Main papers

1) "Theoretical study of contact-mode triboelectric nanogenerators as an effective power source", S. Niu, S. Wang, L. Lin, Y. Liu, Y. S. Zhou, Y. Hu, Z. L. Wang, *Energy and Environmental Sciences* **6** (2013) 3576.

2) "Triboelectric nanogenerator as self-powered active sensors for detecting liquid/gaseous water/ethanol", H. Zhang, Y. Yang, Y. Su, J. Chen, C. Hu, Z. Wu, Y. Liu, C. P. Wong, Y. Bando, Z. L. Wang, *Nano Energy* **2** (2013) 693.

16 Multiple-probe scanning probe microscopes (STM, AFM, KFM): Development and Application

Representative researchers: **T. Nakayama, M. Aono**

Cutting-edge tools: New probe microscopes enable nanoscale measurements

The novel properties of individual nanostructures and nanosystems—the outgrowth of materials nanoarchitectonics--must be characterized using innovative instruments and methodologies. For this purpose, we developed multiple-probe scanning probe microscopes (MP-SPMs) and realized a new class of nanoscale measurements which enable us to perform unique and indispensable nano measurements.

MP-SPMs equipped with individually-driven 2 to 4 probes are used for imaging nanostructures of interest and also for performing multiprobe electrical measurements by direct contact between the same probes and a single nanostructure. With MP-STM, the length of electron mean-free-path of a single-walled carbon nanotube (SWCNT) on SiO_2 was measured to be about 500 nm at room temperature (RT) (Fig.1). MP-STM was converted into a multiple-probe atomic force microscope (MP-AFM) using newly developed tuning fork sensors. The MP-AFM enabled measurements of conductive nanostructures on insulating substrates, i.e., sheet resistance of a graphene flake on SiO_2 was measured to be 2.5 kohm/sq without any gate control of carriers at RT.

High-resolution imaging of an object to be measured, precisely-controlled and reproducible point-contact formation and accurate interprobe distance estimation are all indispensable advantages of MP-SPM against other characterization methods. In addition, MP-SPM measurements require neither pre-processing of the sample such as electrode formation by lithographic processes nor scanning electron microscope (SEM) observations which often damages and changes nanoscale samples. We have recently implemented a non-contact potential mapping function [Kelvin force microscopy (KFM)] in our MP-AFM. In general, four-point probe measurements eliminate affection of contact resistances when an area sufficiently larger than the interprobe distance is dealt with. However, our MP-AFM with KFM fulfilled all the requirements of contact-free electrical measurements even at the nanometer scale.

Main paper

"Development and application of multiple-probe scanning probe microscopes", T. Nakayama, O. Kubo, Y. Shingaya, S. Higuchi, T. Hasegawa, C.-S. Jiang, T. Okuda, Y. Kuwahara, K. Takami, M. Aono, *Advanced Materials* **24** (2012) 1675 (Review paper).

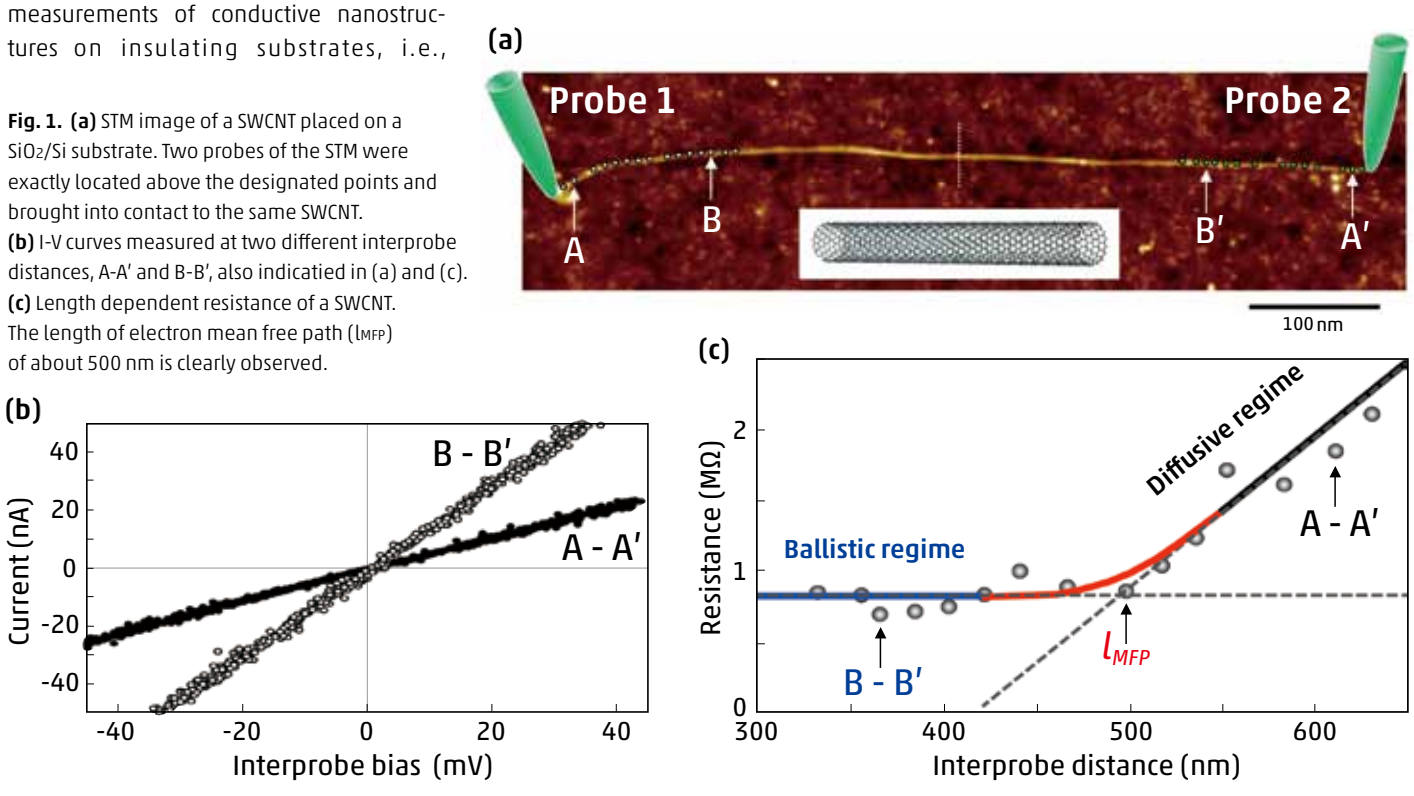


Fig. 1. **(a)** STM image of a SWCNT placed on a SiO_2/Si substrate. Two probes of the STM were exactly located above the designated points and brought into contact to the same SWCNT. **(b)** I-V curves measured at two different interprobe distances, A-A′ and B-B′, also indicatied in (a) and (c). **(c)** Length dependent resistance of a SWCNT. The length of electron mean free path (l_{MFP}) of about 500 nm is clearly observed.

17 Pioneering development of *in situ* TEM techniques for nanomaterial property analysis

Representative researchers: **D. Golberg, Y. Bando**

"TEM" breakthrough: Pioneering techniques allow measurement of nanomaterial properties, insight into atomic structure

Fascinating nanomaterial properties are the subject of a continuous excitement. And the exact knowledge of those, in particular on the individual structure level (that gives the clearest picture free of artifacts), is of key importance as far as the nanomaterial integrations into modern technologies are concerned. Such properties should precisely be studied in order to clarify that the substitution of conventional bulk materials, e.g. Si in electronics, is essential, realistic and profitable. However, in most cases, the *nano*-properties are measured using instruments with no direct access to nanoscale range of dimensions. This has significantly limited the relevance of acquired data since any particular structural features of a nano-object prior/during/after testing have been hidden. Thus, the results could not be directly linked to a particular nanomorphology, crystallography, spatially-resolved chemistry and existing defects. This explains a common scatter of nano-property data reported by various scientific groups which has greatly confused the practical engineers.

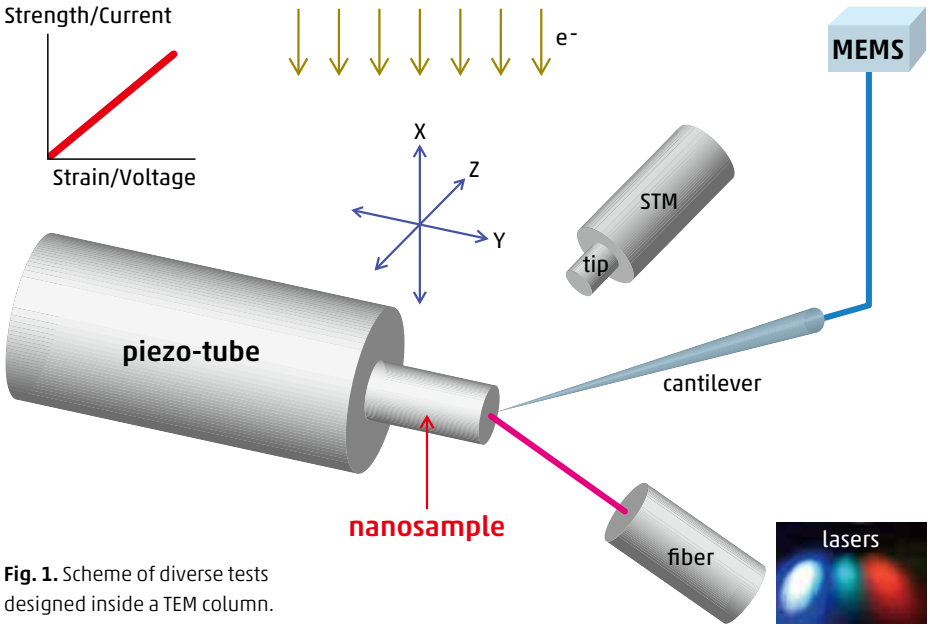


Fig. 1. Scheme of diverse tests designed inside a TEM column.

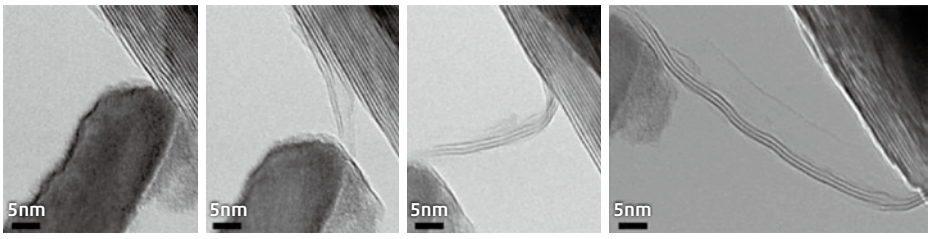


Fig. 2. Consecutive HRTEM images (from left-to-right) revealing the kinetics of a "Scotch-tape" technique for atomic layer peeling; three atomic layers were peeled-off from a layered MoS_2 single crystal under delicate nanomanipulations with the STM metal tip.

Taken all these together, we developed new TEM techniques which allow us to measure *true* mechanical, electrical, thermal and optical properties of nanomaterials, while getting the deepest insights into their atomic structures. Dedicated holders combining the capabilities of a conventional TEM and either an atomic force sensor, or a STM probe, or a laser, become our powerful tools for the analysis of diverse nanotubes, nanowires, nanosheets, and nanoparticles. The key point of all experiments is that the properties have been studied on individual nanostructures under the highest spatial, temporal and energy resolution achievable in TEM and thus can be directly linked to the specifics of every nanomaterial. We became the world-leaders in the *in situ* TEM analysis of elasticity, plasticity, strength and electrical transport of nanoscale objects under direct bending/tensile tests, their *nano*-engineering (thinning, filling/emptying, soldering, doping etc.), and optoelectronic and photovoltaic tests under strains. Such experiments have never been accomplished before by any pre-existing means.

Main papers

1) "Nanomaterial engineering and property studies in a transmission electron microscope", D. Golberg, P. M. F. J. Costa, M. S. Wang, X. L. Wei, D. M. Tang, Z. Xu, Y. Huang, U. K. Gautam, B. D. Liu, H. Zeng, N. Kawamoto, C. Y. Zhi, M. Mitome, Y. Bando, *Adv. Mater.* **24** (2012) 177.
2) "Direct imaging of Joule heating dynamics and temperature profiling inside a carbon nanotube interconnect", P. M. F. J. Costa, U. K. Gautam, Y. Bando, D. Golberg, *Nature Commun.* **2** (2011) 421.
3) "Nanomechanical cleavage of molybdenum disulfide atomic layers", D. M. Tang, D. G. Kvashnin, S. Najmaei, Y. Bando, K. Kimoto, P. Koskinen, P. M. Ajayan, B. I. Yakobson, P. B. Sorokin, J. Lou, D. Golberg, *Nature Commun.* **5** (2014) 3631.

18 Novel porous materials for next-generation high-performance batteries

Representative researcher: **Y. Yamauchi**

Replacing platinum: New method yields nanoporous films for high-performance batteries

Platinum (Pt) have long been regarded as highly useful catalysts in fuel cells. However, the high cost of Pt catalysts, together with the limited reserves of Pt in nature, has been shown to be the major bottleneck for commercial applications. We have developed novel porous electrodes with highly electrocatalytic activity through chemical design.

Direct methanol fuel cells (DMFCs) have attracted great attention recently due to their high energy density, low pollutant emission, low operating temperature, and ease of handling liquid fuel. In view of the strong social demand for the reduced use of rare metals, there have been heightened calls for the development of a technology for securing high functionality with low use of Pt by producing porous structures with larger surface areas (Fig. 1).

Our group has focused on fine controls of compositions, morphologies, and channel orientations which are important factors for design of porous metals. We have developed a route to nanoporous metal films with various pore sizes by a simple electrodeposition method in an aqueous surfactant solution, in contrast to traditional synthetic routes[1),2)]. The pore sizes can be widely tuned by changing the sizes of the used surfactants and adding a hydrophobic aromatic compound as an expander. The Pt atomic crystallinity is coherently extending across several Pt nanoparticles, providing a large number of atomic steps and defect sites. The connected Pt nanoparticles with high crystallinity provide not only high surface area but also the rich atomic steps with concave surface topology, which probably enhanced cleavage of the C–H and O–H bonds in the methanol decomposition. As a result, the electrochemical performance is dramatically enhanced, compared to commercially available Pt catalysts.

Soft-templates used in this study are good candidates as porogen in industry because of their low cost, commercial availability, and biodegradability. The present plating solutions can be reused several times, demonstrating high repeatability. The present process can allow easy preparation of other mesoporous Pt-based alloys, which will be important for realizing higher performance as electrodes in batteries.

Main papers

1) "Electrochemical synthesis of one-dimensional mesoporous Pt nanorods utilizing surfactant-micelle assembly in confined space", C. Li, T. Sato, Y. Yamauchi, *Angew. Chem. Int. Ed.* **52** (2013) 8050.

2) "All-metal mesoporous nanocolloids: Solution-phase synthesis of core-shell Pd@Pt nanoparticles with a designed concave surface", H. Ataee-Esfahani, M. Imura, Y. Yamauchi, *Angew. Chem. Int. Ed.* **52** (2013) 13611.

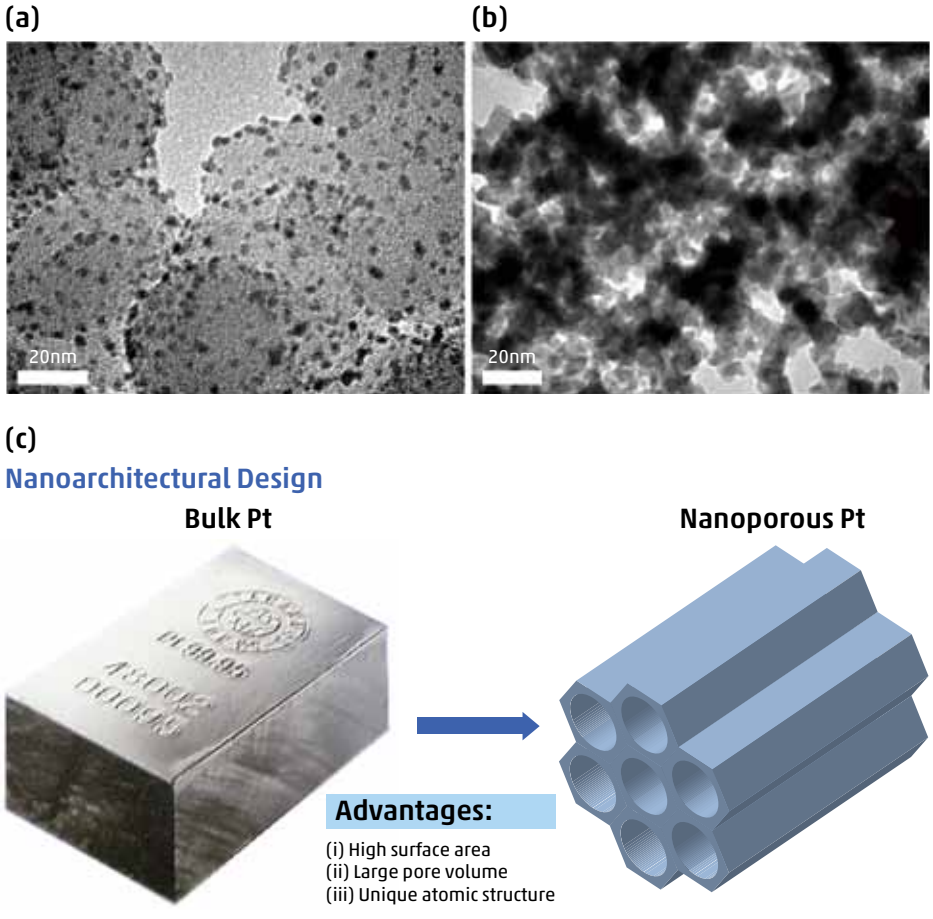


Fig. 1. Transmission electron microscope (TEM) images of commercially available Pt catalysts (**(a)** Pt/carbon composite, and **(b)** Pt black). **(c)** Nanoarchitectural design of nanoporous Pt.

19 Nanoarchitectonic sensing and imaging of Cs in life environment

Representative researcher: **K. Ariga**

Radical clean-up: Fluorescent probe uses molecular interaction to detect caesium with submillimeter accuracy

Various sensing molecules for detection of toxic or useful substances[1)] in our life environments have been explored. Especially, micrometre-level naked-eye detection of caesium (Cs) ions, a major source of contamination upon nuclear plant explosion, has been demonstrated[2)].

As a result of the accident at the Fukushima No. 1 Nuclear Power Plant following the Great East Japan Earthquake of March 2011, a large amount of radioactive substances leaked and contaminated a wide area. Among those substances, caesium 137, will continue to be a source of radiation in the future. The Japanese government has planned and implemented decontamination measures for the region which was contaminated by radioactive substances. However, if the distribution of caesium can be visualized, this decontamination work can be carried out more efficiently, and a reduction in the amount of contaminated waste generated by the decontamination work can also be expected.

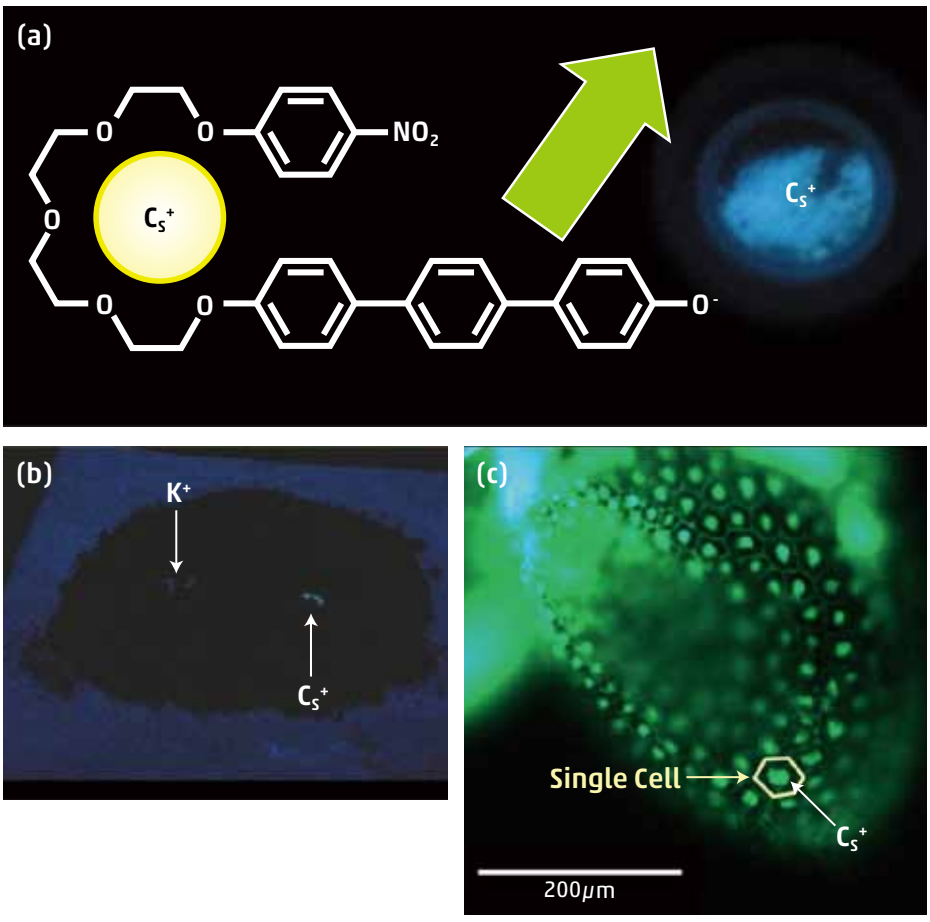


Fig. 1. (a) Caesium detection probe molecule and detection based on fluorescent emission on **(b)** ground and in **(c)** living plant cells.

We have developed a fluorescent probe that detects caesium using supramolecular interaction (Fig. 1(a)). This optical probe emits green fluorescent light when it contains caesium, thereby enabling visual confirmation of caesium distributed on the surface of a solid (Fig. 1(b)). It has higher spatial resolution than the existing methods of detecting radioactive substances, and this makes it possible to visualize the distribution of caesium with submillimeter accuracy. Because this enables selective removal of only the caesium-contaminated spots, a large reduction in the amount of contaminated waste generated by decontamination work can be expected.

The probe was sensitive to caesium concentrations of 1 part per million (Cs^+/K^+). When an alcoholic solution of the optical probe is sprayed on plant leaves grown in the presence of caesium, the distribution of caesium ion within living cells can be visualized under florescence microscopy (Fig. 1(c)) (to be published). Because the developed probe molecule is now a commercialized product, this probe molecule can be widely used for environmental remediation.

Main papers

1) "NMR spectroscopic detection of chirality and enantiopurity in referenced systems without formation of diastereomers", J. Labuta, S. Ishihara, T. Šikorský, Z. Futera, A. Shundo, L. Hanyková, J. V. Burda, K. Ariga, J. P. Hill, *Nature Communications* **4** (2013) 2188.

2) "Micrometer-level naked-eye detection of caesium particulates in the solid state", T. Mori, M. Akamatsu, K. Okamoto, M. Sumita, Y. Tateyama, H. Sakai, J. P Hill, M. Abe, K. Ariga, *Science and Technology of Advanced Materials* **14** (2013) 015002.

20 Highly-efficient plasmonic systems for molecular sensing and energy conversion

Representative researcher: **T. Nagao**

Metals and liquids: Plasmonic systems detect water pollution, convert solar energy

Plasmonics and metamaterials are the new emerging paradigms for materials science which enable us to control the light in nanospace. Through this strategy, we aim at tailoring the remarkable functionality such as extraordinary signal enhancement of molecules, enhanced photocatalytic reaction, and smart solar power harvesting. Also a new platform for photonic quantum computing in nanometer scale is expected.

Increasing interest exists in the field of solar heat energy conversion as well as in molecular sensing. Thanks to the rapid improvements in the bottom-up and top-down nanofabrication techniques in the past decade, dramatic progresses has been achieved in this field. Here in our laboratory, we aim at manipulating the infrared light waves for enhancing the applications in environmental monitoring as well as solar and thermal energy conversion by developing new metallic nanostructures[1]. As the first example, Fig.1 shows an example for the ppt-level single-step selective monitoring of the presence of mercury ions (Hg^{2+}) dissolved in environmental water by plasmon-enhanced vibrational spectroscopy[1]. From natural environmental water from Lake Kasumigaura (Ibaraki Prefecture, Japan), direct detection of Hg^{2+} with a concentration as low as 37 ppt was readily demonstrated, indicating the high potential of this simple method for environmental and chemical sensing of metallic species in an aqueous solution. Secondly, we are now developing novel plasmonic nanomaterials in combination with pn-junction oxide nanocatalyst for efficient photocatalysts optimized for the visible (Vis) solar spectrum[2]. For example, ZnO nanowires or ZnO/TiO_2 core-shell nanowires show high photoelectric transfer with ultraviolet (UV) light illumination and show very little photoelectric transfer with Vis light. However, when the nanowires are in contact with noble metals e.g., when they are loaded with Au or Ag nanoparticles a dramatic increase in photocurrent is observed with Vis light illumination. This means that the UV active materials can be converted into Vis active materials with the presence of plasmon resonance.

Main papers

1) "Monitoring the presence of ionic mercury in environmental water by plasmon-enhanced infrared spectroscopy," C. Hoang, M. Oyama, O. Saito, M. Aono, T. Nagao, *Scientific Reports* **3** (2013) 1175.
2) "Arrays of nanoscale gold dishes containing engineered substructures," J. Wi, S. Tominaka, T. Nagao, *Adv. Opt. Mater.* **1** (2013) 814.

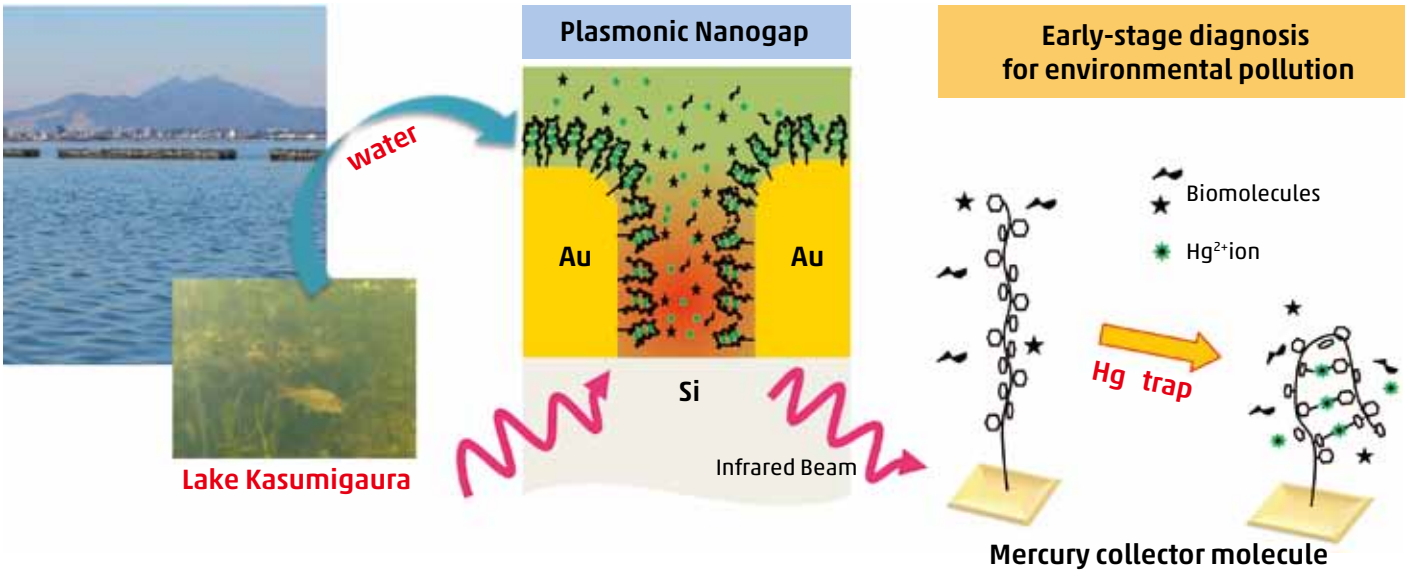


Fig. 1. Schematic illustration of the detection of mercuric ions from environmental water. The change in the molecular structure of the mercury collector is sensitively detected by the infrared absorption signal by the enhanced field of the nanogap plasmon.

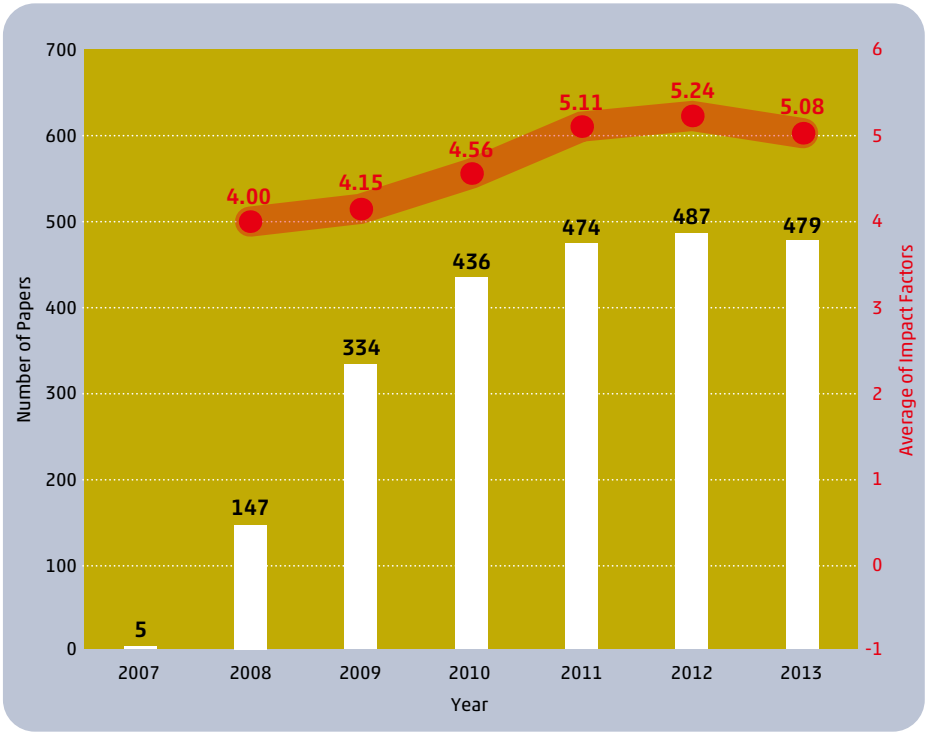
Research Achievements at MANA:The Numbers Tell the Story

Seven years have now passed since MANA was launched in October 2007. During that time, researchers affiliated with MANA have produced a large number of remarkable research results. The following is a statistical overview of MANA's achievements in scientific papers.

Total Number of Papers

2,362

Since the launch of MANA, the number of MANA-affiliated papers has increased year by year, and has now reached a cumulative total of 2,362. The high quality of research at MANA can also be seen in the large number of papers which MANA researchers have published in scientific journals with high impact factors (IF).
In 2013, MANA-affiliated researchers published 479 papers, and the average IF of the journals where those papers were published was on a high level of 5.08.



Journals publishing large numbers of MANA top 1% Papers

Name of journal	Number of top 1% papers
Advanced Materials (15.409)	14
Journal of the American Chemical Society (11.444)	9
Advanced Functional Materials (10.439)	7
Journal of Materials Chemistry (6.108)	6
Nature Materials (36.425)	3
Nano Letters (12.940)	3
ACS Nano (12.033)	3
Chemistry of Materials (8.535)	3

Number in parentheses ( ) show 2013 Impact Factor.

Number of Top 1 % Papers

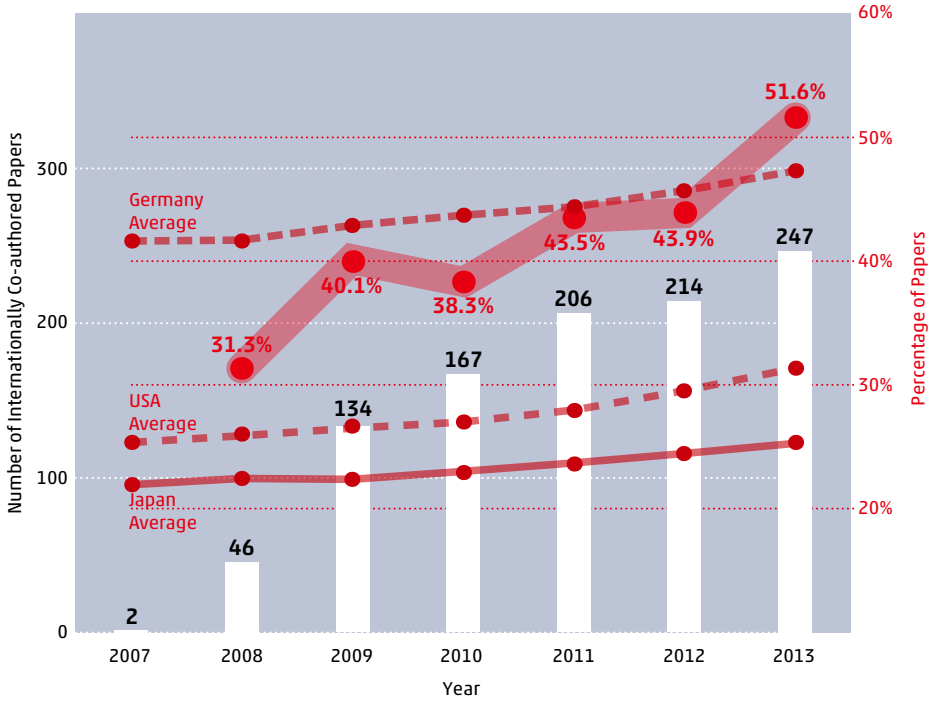
80

Among the 2,362 papers, 80 were "highly-cited" papers (top 1% papers), that is, papers which were in the top 1% for number of citations. Thus, top 1% papers accounted for a high percentage (3.4%) of all published papers. These numbers also show the high quality of research at MANA.

The number of Internationally co-authored papers is increasing annually, and these papers accounted for more than half of MANA's paper productively in 2013. This is a high number and is comparable to Germany, which is one of the world leaders in internationally co-authored papers.
These numbers show the progress of MANA's efforts in cooperative research by researchers from different countries.

Number of Internationally Co-authored Papers

1,016

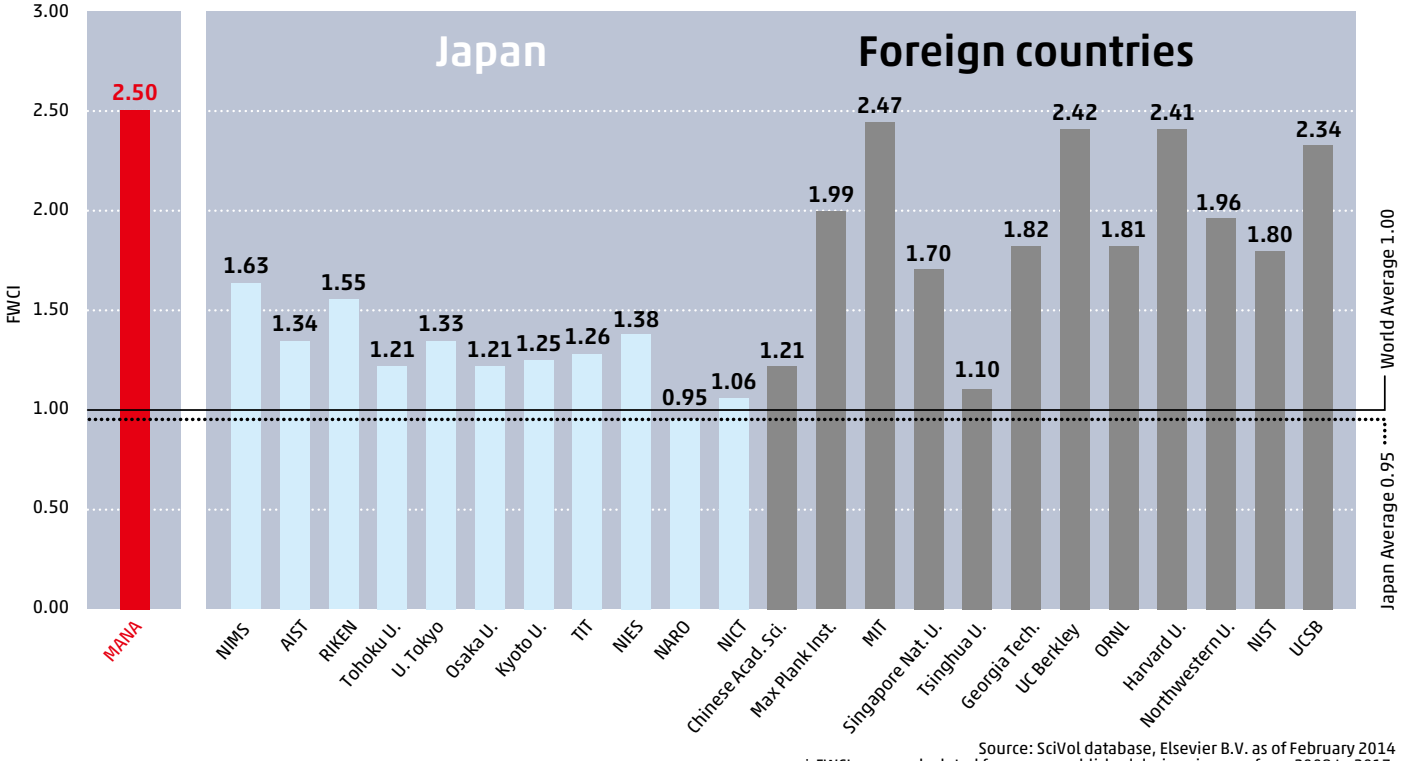


Source of national average : SciVol database, Elsevier B.V. as of June 2014

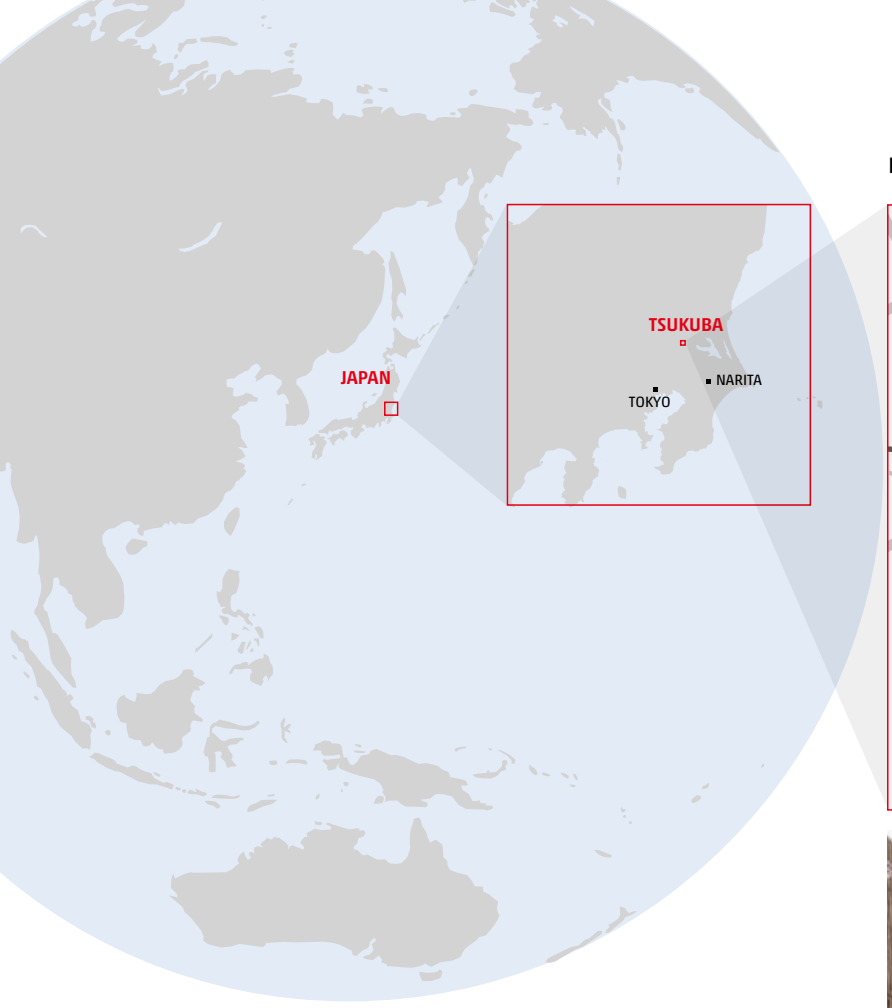
Field-Weighted Citation Impact

2.50

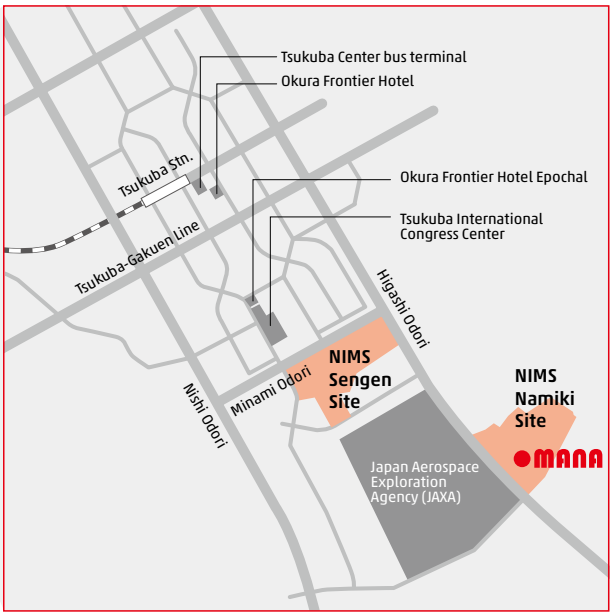
Elsevier recently devised a new indicator called Field-Weighted Citation Impact (FWCI), which adjusts citation counts depending on the level of focus in a given field, thus enabling the comparison of the quality of papers from research centers in different fields.
With an extremely high FWCI of 2.50, MANA's performance is on par with elite universities in the United States.



Source: SciVol database, Elsevier B.V. as of February 2014
＊FWCIs were calculated for papers published during six years from 2008 to 2013.



Detailed Map of NIMS area



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