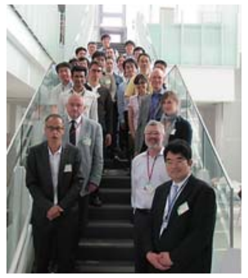
Event Reports

International Workshop on Thermoelectric Research & Thermal Management Technology

On June 28th and 29th 2013, MANA hosted the International Workshop on Thermoelectric Research & Thermal Management Technology. The workshop aimed to share cutting-edge research results on thermoelectric materials and thermal management technology in order to improve the current state of affairs, where more than two-thirds of primary energy input is converted into waste heat that is unused and exhausted into the atmosphere. Top researchers inside and outside MANA took part in the workshop, which consisted of a tour of MANA labs on the first day and 12 oral presentations on the second day.


Group photograph of the workshop participants

Summer Science Camp 2013

For three days (August 6th-9th 2013), MANA held a program as part of "Summer Science Camp 2013," which is a camp for high school students hosted by the Japan Science and Technology Agency. The camp consisted of programs where universities, public research institutions and private companies involved in advanced research invited students during the summer break and introduced them to cutting-edge science and technology. Twelve high school students from all over Japan joined our program. They participated in trainings, which allowed them to experience the nanoscale world through observations using an electronic microscope and development processes in a clean room. In addition, they also attended an exchange meeting with young international researchers, which offered the opportunity for students to deepen understanding of nanotechnology and international society.


A clean room experiment

2013 WPI on-site visit

MANA received the 2013 on-site visit under the World Premier International Research Center Initiative. The program director, program officers, working group members, MEXT officials and other involved individuals visited MANA. President Aono outlined the central points of MANA, principal investigators gave presentations about their research, and a poster session as well as a general discussion was held. Furthermore, there was an exchange of opinion regarding initiatives at the end of the support period. Throughout the visit, MANA was shown to be a growing hub in the international network of materials science research.


Opinion exchange at the on-site visit

Newly Appointed Researchers

◆MANA Scientist◆


Song-Ju Kim

◆ICYS-MANA Researcher◆


Yohei Kotsuchibashi


Fengxia Geng


Huynh Thien Ngo


Xi Wang

Information

Special issue of *Langmuir* on Interfacial Nanoarchitectonics published

Langmuir, a journal published by the American Chemical Society (ACS), released the Interfacial Nanoarchitectonics Special Issue (Vol.29, No.24). Classified under "Chemistry" in the Thomson Reuters database of academic journals, *Langmuir* has a high impact factor of 4.186. On the occasion of this special issue, 34 out of the 49 papers which were received from all over the world, were from outside MANA. This shows that the concept of nanoarchitectonics, of which MANA is the proponent, has been widely adopted across the globe.

Special issue of *Langmuir* on Interfacial Nanoarchitectonics

Awards

Principal Investigator Francoise Winnik receives the Society of Polymer Science Japan's International Award

Principal Investigator Francoise Winnik from MANA won the Society of Polymer Science Japan (SPSJ)'s International Award (project awarded: Studies on Thermo-responsive and Amphiphilic Polymers), and the award ceremony was held at the Society's 62nd annual meeting at the Kyoto International Conference Center on May 29th, 2013.


Prof. Winnik receiving an award from SPSJ President Prof. Akashi

The SPSJ International Prize was established in order to recognize the efforts of foreign polymer scientists who have contributed to basic and applied science in the fields of polymer science or engineering for many years and who have an outstanding track record of exchange with Japanese researchers.

Independent Scientist Genki Yoshikawa receives a Tsukuba Encouragement Prize

On September 3rd 2013, the Science and Technology Promotion Foundation of Ibaraki announced a laureate of a Tsukuba Encouragement Prize (Young Researchers Division), which was received by Independent Scientist Genki Yoshikawa from MANA. Aiming to promote creative research activities, this prize honors researchers involved with science and technology in Ibaraki Prefecture who have obtained significant research results. Dr. Yoshikawa was awarded the prize for research entitled "Development of Ultrahigh-Sensitivity Nanomechanical Membrane-type Surface Stress Sensors."


Dr. Genki Yoshikawa

CONVERGENCE No. 15, Eng. Ed., issued on October, 2013

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"CONVERGENCE" is the keyword used to symbolically describe the entire project of MANA, where outstanding researchers from around the world assemble and converge in the "melting pot" research environment to bring together key technologies into nanoarchitechtonics for the creation and innovation of new functional materials.

International Center for Materials Nanoarchitectonics (MANA)

No.15
Oct.2013

CONVERGENCE

"The Secret of All Those who Make Discoveries is that They Regard Nothing as Impossible"
— J. Georg Bednorz

From Small Things Do Big Things Grow
— Joel Henzie

"Highly Visible" New Research Building

"The Secret of All Those who Make Discoveries is that They Regard Nothing as Impossible"

J. Georg Bednorz

Physicist J. Georg Bednorz, born in 1950 in West Germany and educated at the University of Münster, earned his Ph.D. from the Swiss Federal Institute of Technology (ETH) in 1982, prior to joining IBM Research in Zürich. Dr. K. Alex Müller enlisted him to work together in search of superconductivity* at higher critical temperatures; disappearance of electrical resistance in the superconducting state was restricted then to extremely low temperatures. In 1986 the two scientists produced a lanthanum/barium/copper oxide compound having a critical temperature of 35 K (-238°C), substantially warmer than for other materials. Dr. Bednorz was awarded the Nobel Prize for Physics in 1987, shared with Dr. Müller, for this discovery.

Dr. Bednorz, now IBM Fellow Emeritus at the Zurich Research Laboratory, spoke at MANA International Symposium 2013 – Nano Revolution for the Future – on "High Tc Superconductivity, after a Quarter Century, a Technology Ready to Take Off." CONVERGENCE interviewed him during his visit.

Road to Nobel Prize

—Can you tell us more about your Nobel Prize-winning research? There are risks when exploring, but in your case why did you make this discovery?

What brought us to work on these materials for high Tc superconductivity was simply the fact that we had collected knowledge on these oxides. The IBM lab in Zürich had a long-held tradition for this from the 1960s, to work on a very specific class of materials which showed interesting phenomena with respect to structural phase transitions and physical properties at low temperatures. For instance, ferroelectricity could be induced by chemically manipulating these compounds; some even exhibited metallic conductivity. Many different properties were found in one particular class of materials with perovskite structure.

Zürich had different groups in solid-state physics working on magnetic properties or structural aspects. We investigated local properties, like the shape of simple building blocks of the perovskite structure – the metal-oxygen octahedra – and, for example, how they react upon different doping. They could deform spontaneously if a compound's chemical composition was changed.

This led to the idea and we could manipulate conducting oxides in a way that they would show these spontaneous distortions; and we believed such distortions, when dynamically interacting with the electrons, may lead to superconductivity and at temperatures hopefully a bit higher than those obtained for intermetallics and alloys. But we could never be sure whether we would be successful or not since there was no theoretical background pointing in this direction.

In a way, however, this idea was extremely helpful as it reduced the possible chemical elements included in our research. As we carried out the synthesis of new materials, it guided us to cuprates... and "we hit land" – discovering hitherto-unknown "new world" of high Tc superconductive materials.

Superconductivity Research

—After winning your Nobel Prize, you are still involved in superconductivity. Furthermore, there are research activities by others, e.g., discovery of iron-based high Tc superconductors. How do you think research and engineering should proceed in realizing practical applications?

For research of new superconductors, the dilemma of having no guidance from the theoretical side still exists. It is all left to new unpredicted discoveries, new compounds... but I realized upon researching the field that organic superconductors had been forgotten. I recall that when we were working on the oxides, there were also others involved in a series of organic superconductors, with transition temperatures around 1 Kelvin. Within few years, Tc had reached levels of 11 or 13 Kelvin.

But after our discovery became known, everyone was joining the research field of oxide superconductors. Maybe we should take another look at organics again, perhaps artificial superconductors produced with the help of nanoarchitectonics, for furthering research.

With respect to research in the field of applications, in the past, very important contributions have been made more from the engineering side. We still need to develop new methods of deposition for the superconducting materials, less expensive yet enabling faster mass production of superconducting wires.

There too is the issue of how to get still higher critical current densities. For this, it is important to understand the response of superconductors to a magnetic field: how to introduce and control defects which are suited to efficiently pin magnetic flux lines. Because any movement of flux lines under the influence of a flowing current will dissipate heat and reduce the critical current.

Albeit there is also the ever-existing discussion about the pairing mechanism, an issue not only for theoreticians but also for experimentalists upon choosing the right experiment to find the prove for the pairing mechanism.

Risk-taking is Essential

—How does your home institution approach human resource building? Does IBM have some sort of formula when nurturing young researchers?

Younger people are Master's/Ph.D. students working with established researchers who share different social activities, organized by the people themselves, and supported by the lab management. For example, I was part of the "Wednesday night IBM soccer team" in one "Hobby Club" section. The mix of scientific and social interaction played an important role in my career. The community spirit makes research life really enjoyable!

We had people from all over the globe. Nevertheless, what counts is the diversity within the research population. IBM Zurich today has roughly 38 different nationalities. By promoting exchanges across borders, cultures and disciplines it appears MANA is going in the same direction.

—Recent years have seen an apparent decline in young Japanese researchers wishing to go overseas. How can "forthcomingness" be drawn out?

I think the WPI approach to internationalization is helpful, because as a first step the young researchers here can get in touch with foreign counterparts, PIs and visiting scientists from overseas on their own home ground, in their own (cultural) setting. Thus WPI brings Japanese researchers a step closer to going overseas. But beyond this cultural barrier, I can only speculate, but to me it seems that young people today can't foresee their future, afraid reasonable positions will already be filled when they return to Japan.

MANA and the reputation it has built should enable researchers to go overseas yet still obtain attractive positions upon returning home. That being said, going abroad in any case poses a certain risk.

—In your case, although it was across borders rather than seas, you must have had a similar experience.

Yes, it was like jumping into cold water when during my studies I spent a few months as a summer student at the IBM Zurich Research Laboratory. You're absolutely correct. This move was not only to a foreign country but also from university life into a serious research environment. Especially for a student at my stage, with no experience in real lab life, this was a challenge. But I wanted to gain a new experience. I entered a new field where I took some risks and even attempted my own approach in solving a problem. New ideas may sometimes mean failure of an experiment or even a project, but if you realize you are capable of learning from such failures to gain new insights, it will improve your confidence. One must learn to lose fear of failure, have confidence in one's own capabilities, in order to take a certain risk or start something completely new having an open outcome. Talented researchers will keep their eyes open to detect weaknesses and uncertainties in their respective scientific fields, or be inspired by limits of existing technologies.

Out of the Blue

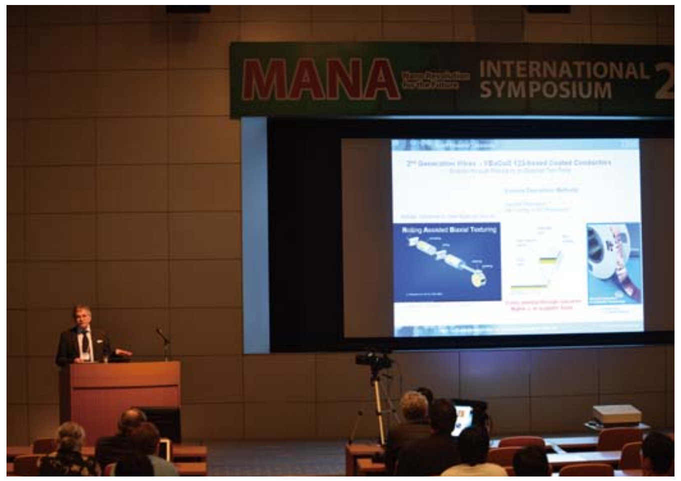
—What is your perception concerning MANA and WPI initiative?

Generally, it was a great idea that WPI's originators decided to strengthen international connections both by engaging Japan scientists internationally and bringing overseas scientists to work in Japan. I myself have experienced different cultures. So I worked with Japanese scientists for a couple of decades.

Some of those collegues contributed very successfully to progress in different projects because to realize some ideas the "Japanese mentality" was needed – a mentality perhaps amiss in certain of my collaborators. While they were frequently reluctant to do what I proposed, my Japanese colleagues essentially replied, "Yes, can do!"

However I am concerned about the WPI program's time-frame. I sense tension within WPI organizations, because of uncertainty about the five-year term being extended or not. My experience is that what really counts, is continuity of support, not just a big research budget.

I assert that "discoveries and technological breakthroughs often come out of the blue" and they come because of the special people involved, like those described by Justus Liebig, to quote: **"The secret of all those who make discoveries is that they regard nothing as impossible."** This requires a research culture in which scientists are free to develop unconventional ideas rather than being forced to develop under a fixed timetable. I hope MANA and all other WPI centers succeed in creating an open, relaxed atmosphere, an environment where people can think in depth as well as even against the mainstream – and thus will achieve their ambitious goals.



Special lecture at MANA International Symposium 2013

(Interviewer: C. Ames POMEROY)

*By definition, superconductivity is the phenomenon in which resistance of materials decreases to completely zero, a promising characteristic which will be the dream technology to solve the present energy problem, if it is realized at normal temperature. Superconductivity had been seen only at low temperatures near absolute zero before the discovery of high temperature superconductors by Dr. Bednorz and Dr. Müller. The discovery had the highest level of impact not only because the critical temperature Tc dramatically increased but also because the new superconductors were "ceramics" which nobody had ever expected for superconductors.

From Small Things Do Big Things Grow

Joel Henzie
Independent Scientist, MANA

Dr. Joel Henzie is an Independent Scientist in MANA, from the United States of America. He spent four years as a postdoctoral researcher at UC Berkley under Professor Peidong Yang, an inorganic nano-materials researcher with an exceptional international reputation. He came to MANA last fall and his energetic work included a contribution to *Nature Materials, Small* and *PNAS*. We asked him about his research life in Japan and future prospects.

Dr. Henzie, what made you decide to come to Japan after spending many years in the U.S. conducting research?

I am asked this question a lot! During my doctoral work at Northwestern University I heard a lot about NIMS through various colleagues, and a number of NIMS scientists visiting the US. After my postdoctoral work at UC-Berkeley, I decided that I wanted to live abroad and continue the fundamental side of my research on self-assembly, and simultaneously take this work in a much more applied direction. NIMS provides a number of unique opportunities for me, both in the strong interactions with both academia and industry, in addition to the level of scientific instrumentation located here in Tsukuba. Also, from my experience and initial impressions I think institutions here are more reliable in their commitment to support the scientific research of early-career scientists.

You appear to have the perfect profile for a MANA researcher, with its "Melting Pot" approach. How do you find the setting here?

I hope that I can contribute something to the culture at MANA! This place has a lot of opportunities to offer researchers who are willing to reach out and explore the full spectrum of work being done both in NIMS and the larger research community in Tsukuba. I like to think that the type of person who comes here will realize this and take advantage of the environment. As a new researcher, I have initially been consumed with the task of building a new laboratory from scratch. This is always a challenge, but I think I was prepared in part because my PhD advisor (Teri W. Odom) was an assistant professor during the bulk of my doctoral work. From her I learned a lot about the process of starting a fully functioning research lab, and I think these lessons have become invaluable in getting my work moving along quickly.

Independent Scientist
Dr. Joel Henzie
(Plasmonics, Self-assembly, Shape-controlled synthesis)

2012 - Present	Independent Scientist, MANA, NIMS
2008 - 2012	Postdoctoral Researcher, Department of Chemistry, UC-Berkley, USA
2003 - 2008	Ph.D., Northwestern University, USA
1996 - 2000	B.Sci., University of Nebraska-Lincoln, USA

Can you tell us more about your research?

In my laboratory we are learning how to construct large-scale, ordered three-dimensional (3D) materials that have interesting and useful properties. We employ a process called self-assembly, which takes disordered parts or "building-blocks" that we essentially program via chemistry with the information to self-construct themselves. Once we let them go, they respond to a range of interactions and driving forces and assemble into complex architectures. So in a sense, we are having Nature do the work to build these structures that would be impossible or too costly to make with conventional manufacturing processes.

An important component of my work is the design of these building blocks. We use a combination of chemical and colloidal synthetic methods to make precisely shaped particles composed of either metal or semiconductor materials. I prefer to use colloidal methods as opposed to nanofabrication since they are easily scalable in an industrial setting. Once we make a new material, we use both shape and surface chemistry to assemble these nanoparticles into 3D superlattices. Since we cannot always predict the structures we make experimentally, we are simultaneously developing new theoretical tools to understand the mechanism of nanoparticle growth in addition to the self-assembly process.

These 3D superlattice materials are interesting because they often have vastly different optical, electronic and chemical properties compared to the same material in bulk form. So the other component of my research efforts seeks practical applications for these superlattice materials. For example, superlattices composed of gold or silver nanoparticles have very unusual optical properties, and we are already making new kinds of optical lenses and other optical components that have many key advantages over conventional optics. Additionally, we are also aiming to develop new kinds of self-assembled batteries and chemical catalysts with improved physical properties that are better for the environment.

Sounds like a lot of patents will be entailed. Do you see yourself rich and famous as a result? Or even winning the Nobel Prize?

[Laugh] I doubt anyone at this early stage in their career should be making plans to win a Nobel. The truth is that scientific research requires perseverance and a whole lot of humility, and those who excel in these technical fields somehow find rewards that are perhaps far outside the boundaries of extraordinary wealth and/or real fame. I cannot describe exactly what I mean here, because the motivation to do research is different for each person. But, anyway, I do think it is reasonable to think that the new kinds of materials my lab is developing at MANA will be useful in the future. But I also hope that our commitment to both experimental and theoretical understanding of materials systems will have societal value even beyond what is patentable.

"Highly Visible" New Research Building

The WPI-MANA research building at the NIMS Namiki site, where MANA is located, was designed with the goal of increasing opportunities for researchers to meet each other. Since opening in May 2012, WPI-MANA has completely changed the research style of MANA researchers and has increased international research exchange even further. Here, the new research building is introduced from the viewpoint of the effects of the spatial design on research activities.

■ Collegial offices

Occupied by researchers from many different fields, the offices on each floor are large rooms without internal walls. This naturally promotes interdisciplinary research exchange, and creative research is born through the fusion of different fields.

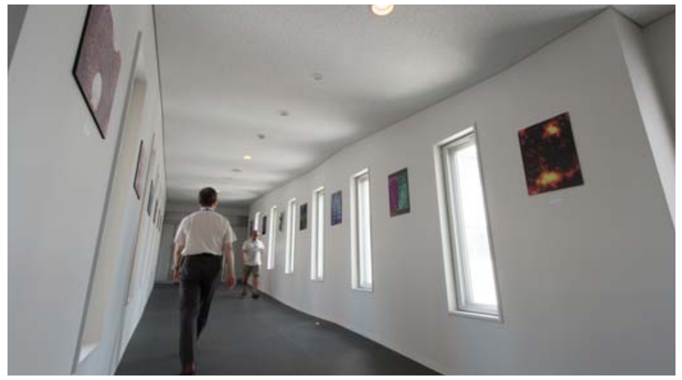
■ Transparent laboratories

The physical transparency of the building's laboratories, with walls and hallway doors made of glass, is also emphasized. This allows researchers, as they pass by a laboratory, to see what experiments are being conducted inside and also brightens the building's interior.

■ Forum for nanoarchitectonics

The auditorium was designed as a space for friendly competition. Its design, which is conductive to lively discussion, includes a large screen and amphitheater-style seating equipped with desktop microphones.

■ Inspirational hallways



Many artistic science pictures provided by MANA researchers, such as electronic microscope images and CG-generated patterns of nano-structures, are displayed on the walls in the building's corridors. The purpose of these images is to stimulate researcher's creativity and to promote interdisciplinary exchange.

■ Everywhere melting pot

In the design of the new research building, Dr. Ushioda, the president of NIMS, requested that the design promote interaction between researchers as they are headed to their laboratories and offices. Based on this concept, the entire research building was designed as a 'melting pot.' For example, the space linking the WPI-MANA building to the adjacent Nano GREEN building—a bright, sunlit atrium made of glass—is also used as a space for interaction. In addition to recreation and relaxation activities, this space is used throughout the day by groups of researchers engaged in discussion and by individual researchers absorbed in the materials they are reading or writing.

Oral Nanotherapeutics for Intractable Diseases

Yukio NAGASAKI
MANA Principal Investigator,
Nano-Life Field
University of Tsukuba

Due to dietary changes, number of patients of colon diseases such as ulcerative colitis or Crohn's diseases are increasing significantly in addition of colon polyp and colon cancer in our country. The ulcerative colitis has been specified as one of an intractable disease in our country. Total number of patients of the ulcerative colitis is more than 100,000 and increasing by 8,000 every year.

Inflammatory bowel disease (IBD), including Crohn's disease and ulcerative colitis (UC), affects millions of patients worldwide. Because the etiology and pathogenesis of IBD are not well understood, it is considered an intractable disease. The intestinal mucosa of patients with IBD is characterized by reactive oxygen species (ROS) overproduction and an imbalance of important antioxidants, leading to oxidative damage. Self-sustaining cycles of oxidant production may amplify inflammation and mucosal injury. In several experimental models, antioxidant compounds and free radical scavengers have improved colitis. However, these compounds are not completely effective due to a nonspecific drug distribution, low retention in the colon, and side effects. If antioxidant compounds are specifically targeted to the diseased sites and effectively scavenge excessive generated ROS, they represent a safe and effective treatment for IBD. We have designed novel nanotherapeutics based on self-assembling amphiphilic block copolymer. The amphiphilic block copolymer, which we have newly designed, possesses stable nitroxide radicals as a side chain of its hydrophobic segment. The oral administration of the self-assembled nanoparticle (abbreviated as RNP^O, Figure 1)[1] accumulates specifically in the colon due to its size and high colloidal dispersion stability, which prevents aggregation in harsh GI tract conditions. It is important to note that no blood absorption is observed by oral administration of RNP^O, which causes no adverse effect to entire body. RNP^O significantly accumulates in colon mucosa and scavenges excessively generated ROS to result in suppression of inflammation. Consequently, RNP^O is more effective in reducing inflammation than low-molecular-weight nitroxide radical compounds or commercially available mesalamine (Figure 2)[2]. RNP^O might be developed for treatment of patients with ulcerative colitis. Anti-oxidative polymer nanoparticle based on newly designed nanoarchitechtonics is promising as novel category of advanced nanotherapeutics.

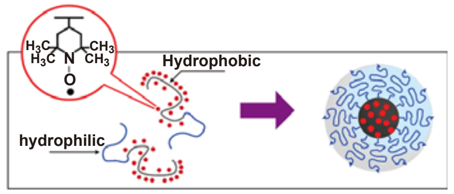


Figure 1 Preparation of Redox Active Nanoparticle for Oral Nanotherapeutics.

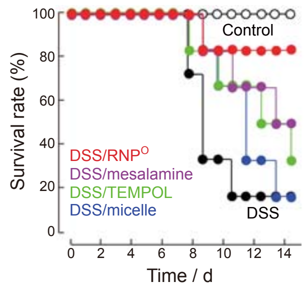


Figure 2 Survivals of Ulcerative Colitis Model Mice after Oral Drug Treatments.

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2. a)Long Binh Vong, Toru Yoshitomi, Kazuya Morikawa, Shinji Saito, Hirofumi Matsui, Yukio Nagasaki, Oral nanotherapeutics: Effect of redox nanoparticle on microflora in mice with dextran sodium sulfate-induced colitis, *Journal of Gastroenterology*, in press. (doi: 10.1007/s00535-013-0836-8). b) Sha Sha, Long Binh Vong, Pennapa Chonpathompikunlert, Toru Yoshitomi, Hirofumi Matsui, Yukio Nagasak, Suppression of NSAID-induced Small Intestinal Inflammation by Orally Administered Redox Nanoparticles, *Biomaterials*, in press(doi: 10.1016/j.biomaterials.2013.06.032).

On-Demand-Type Device with Switchable Functions Responding to the Needs Realizes Diverse Functions of Diode, Switch, Brain-Type Memory, Etc.

Kazuya TERABE
Group Leader,
Nano-System Field

Semiconductor devices, represented by transistors, are continuing to improve at a rapid pace. However, there are darkening signs regarding their future development. To continue to improve the performance of electronic information devices in the future, the development of devices based on new operating principles is also important. In our research, an on-demand-type device based on the new concept of switching multi-functions in response to the user's needs was developed. In conventional semiconductor devices, it was difficult to switch the functions of a device once the device was constructed and configured in an integrated circuit. By using the on-demand-type device developed, it is possible to reduce the number and size of devices in integrated circuits, and furthermore, develop programmable circuits which make it possible to switch the functions of integrated circuits when necessary.

Our on-demand-type device is fabricated using a stacked structure comprising a mixed conductor WO_{3-x}, in which oxygen ions (oxygen vacancy) and electrons can move in the solid, arranged between a pair of metal electrodes (Fig. 1). By using the electrochemical reaction and mobility of oxygen ions in the mixed conductor, which depend on the size and frequency of repetition of input electrical signals, it is possible to change the electrical conductivity at the interface between the mixed conductor and the electrodes. We successfully realized diverse functions by utilizing these changes in electrical conductivity properties, and also achieved switching of those functions.

The developed device not only has the functions of a diode, switch, etc., which can also be found in conventional semiconductor devices, but also displays the functions of short-term memory and long-term memory, which are characteristics of the human brain (Fig. 2). These multi-functions are switchable by controlling the applied bias condition. We propose this on-demand-type nanoionic device with a range of neuromorphic and electrical multifunctions that may allow the fabrication of configurable circuits, brain-type memories and digital–neural fused networks in one device architecture.

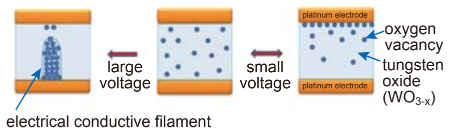

Figure 1 Structure of the on-demand-type device and the principle of its operation.

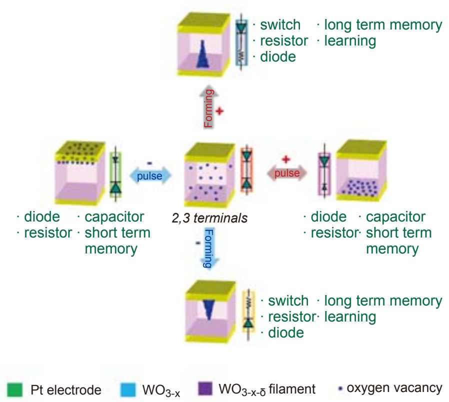

Figure 2 Diverse functions of the on-demand-type device and method of switching those functions.
Electrical conductivity in the interface is expressed by the marks of diode and resistance in their sizes.

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Characterization of Interfacial Water Structure at Polymer Electrolyte Membrane (Nafion®) by Sum Frequency Generation Spectroscopy

Hidenori NOGUCHI
MANA Scientist
Nano-Power Field

Nafion® is a perfluorosulfonate ionomer (PFSI), which contains a fluorocarbon backbone with pendant side chains that terminated with a sulfonate groups and the most commonly used in proton exchange membrane fuel cell (PEMFC) as membrane and ionomer. The hydrophobic properties of the fluorocarbon backbone and the hydrophilic properties of the highly ionic sulfonate site, provides such unique structures. The hydrophilic domain of the PFSI facilitates the uptake and transport of water and proton which strongly affect the performance of a PEMFC. Thus, understanding of the hydration behavior of PFSI membrane is not only a subject of chemical interest but also of great importance for the development of PEMFC.

Sum frequency generation (SFG), in which two photons of frequencies ω_1 and ω_2 generate one photon of sum frequency ($\omega_3=\omega_1+\omega_2$), is one of second order nonlinear optical processes and do not take place in media with inversion symmetry under the electric dipole approximation but only at the interface between these media where the inversion symmetry is necessarily broken. By using visible light of fixed wavelength and tunable IR light, SFG spectroscopy can be surface sensitive vibrational spectroscopy and, therefore, is one of the most powerful techniques to investigate the structure of water molecules at interfaces.

Relative humidity (RH) dependent structure of water at PFSI membrane surface was studied for the first time by SFG spectroscopy (Fig. 1). The behaviors of water molecules inside of PFSI membrane against various RH have been investigated by several groups. It was known that structure of water will change from "ice-like" to "liquid-like" by increasing RH in bulk membrane. At PFSI membrane surface, however, we found that at low RH, most of the water molecules at PFSI surface exist in the proton channel, i.e. sulfonate site to form a "liquid-like" structure. When the RH was increased, water started to adsorb also at the fluorocarbon site of PFSI surface, which is very has a hydrophobic properties, and starts to form a "ice-like" structure (Fig. 2). Compared to bulk, surface or interface has kept many different structures and properties, thus, it is important to obtain the information about the surface and interface selectively.

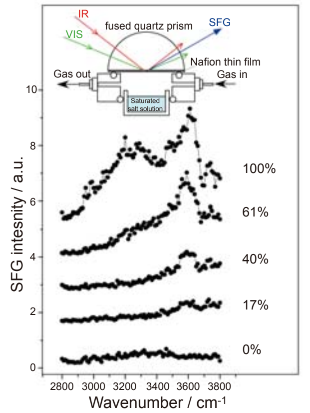

Figure 1 SFG spectra of water at Nafion/water vapor interface under various RH conditions.

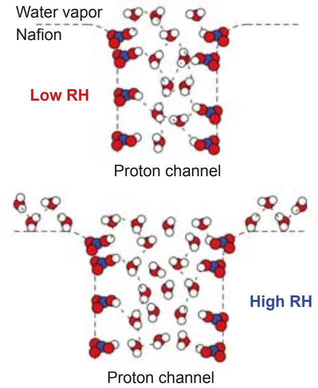

Figure 2 Model of interfacial water structure at Nafion/water vapor interface under low (Top) and high RH (Bottom) conditions.

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2. Hidenori Noguchi, Kento Taneda, Hiroshi Minowa, Hideo Naohara, and Kohei Uosaki *J. Phys. Chem. C*, **114(9)**, 3958-3961 (2010).

Revealing the Anomalous Tensile Properties of WS_2 Nanotubes by in situ Transmission Electron Microscopy

Dai-Ming TANG
ICYS-MANA Researcher

WS_2 nanotubes consist of covalently bonded S-W-S coaxial shells which are weakly joined by the van der Waals forces, similar to the layered structure of carbon nanotubes (CNTs) and boron nitride nanotubes (BNNTs). Compared with the C and BN counterparts, WS_2 nanotubes have a substantially different atomic structure, that is, each shell consists of three atomic layers rather than has a simple planar sp^2 structure. It is fundamentally interesting to have a comparative investigation on the structure dependent mechanical properties, and critically important to understand the tolerance and influences of defects on the mechanical properties for their practical applications.

In this work,[1] we used an in situ transmission electron microscopy (TEM) method to investigate the tensile properties of the multiwalled WS_2 nanotubes. Our work enables direct correlation between the mechanical properties and the fracture mechanisms at the atomic level. A typical tensile test result is demonstrated in Figure 1. Initially, the nanotube has an outer diameter of ~ 58.2 nm and a length of ~ 1.6 μm. After tension, the total length of the sample was increased to ~ 2.1 μm. Obviously this nanotube fractured in a "sword-in-sheath" manner, with its outer part broken and its inner part pulled out. However, as shown in a high-resolution TEM image, three tubular shells fractured simultaneously, rather than only the outermost shell. We found that the specific structures, such as the inter-shell crosslinking and inverted cone-shaped caps had important influences on the tube mechanics. It is interesting that due to the regarded "imperfections", most of the present WS_2 nanotubes fractured through multiple-shell breakage rather than via a single-shell failure, which resulted in a much higher loading force than the thin WS_2 nanotubes with almost "defect-free" structures studied previously.

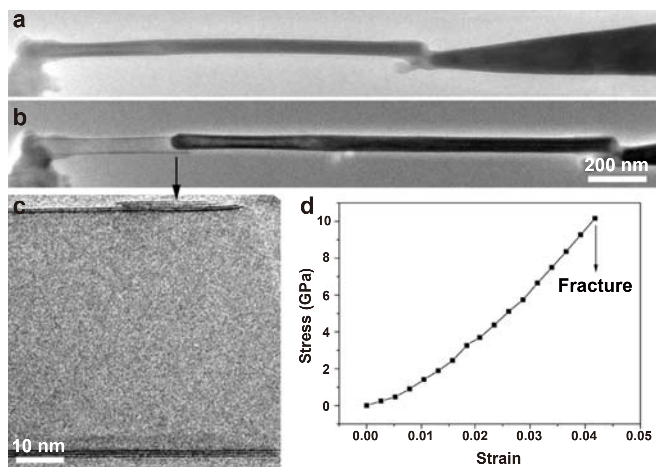

Figure 1. Tensile testing of an individual WS_2 nanotube. (a-b) TEM images of the nanotube before and after the test. (c) HRTEM image of the fractured end, demonstrating that there are three external layers broken. (d) Strain-stress curve. The stress increased with the strain linearly, until the abrupt fracture at a strain of ~4.0 % and a stress of ~8.9 GPa.

References
1. D.-M. Tang, *et al. Nano Lett.* **13**, 1034, (2013).