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.

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 science.

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, NEXT officers 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.

Newly Appointed Researchers

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<tr>
<th>MANA Scientists</th>
<th>CYS-MANA Researchers</th>
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<tr>
<td>Seng-Ju Kim</td>
<td>Yukie Kato</td>
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<td>Yohei Kotsuchibashi</td>
<td>Tengui Geng</td>
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<td>Huuy Tin Ngv</td>
<td>Xi Wang</td>
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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 4.188. 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.

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.

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 Ultra-sensitive Nanomechanical Membrane-type Surface Stress Sensors.”

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MANA’s Research Outcome

Oral Nanotherapeutics for Intractable Diseases — Yukio NAGASAKI
On-Demand-Type Device with Switchable Functions Responding to the Needs Realizes Diverse Functions of Diode, Switch, Brain-Type Memory, Etc. — Kazuya TERABE
Characterization of Interfacial Water Structure at Polymer Electrolyte Membrane (Nafion®) by Sum Frequency Generation Spectroscopy — Hiidenori NOGUCHI

“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 nanoarchitectonics for the creation and innovation of new functional materials.

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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

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 framework – and, for example, how they react upon different doping. They could deform spontaneously if a compound’s chemical composition was changed.

These superconducting 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 the lab management for internmetallics 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 copperates... 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 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 grounds. New (outgoing) flows 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 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.

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 Japanese 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 colleagues contributed very successfully to progress in different projects because they could properly realize some ideas – the “Japanese mentality” was needed – a mentality perhaps amiss in some 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 reallycounts, 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: “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.

LEADER’S VOICE

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.

Special lecture at MANA International Symposium 2013

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 global 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.

“...”

Interviewer: C. Ames POMEROY

CONVERGENCE Vol. 15 October 2013

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“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.

Forum for nanoarchitectonics

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

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.

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 Berkeley 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 (Tel 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 my work moving forward.

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 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 entitled. 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.
Oral Nanotherapeutics for Intractable Diseases

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 diseases (IBD), including Crohn’s disease and ulcerative colitis (UC), affects millions of people 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 antioxidant mediators, leading to oxidative damage. Self-sustaining cycles of oxidative production may amplify inflammation and mucosal injury. In several experimental models, antioxidant compounds and free radical scavengers have improved colons. However, these compounds are not completely effective due to a non-specific 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 nitrooxide radicals as a side chain of its hydrophobic segment. The oral administration of the self-assembled nanoparticle (abbreviated as RNPO), Figure 1, accumulates specifically in colon mucosa due to its size and high coloidal 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 RNPO, which causes no adverse effect to entire body. RNPO significantly accumulates in colon mucosa and scavenges excessively generated ROS to result in suppression of inflammation. Consequently, RNPO is more effective in reducing inflammation than low-molecular-weight nitrooxide radical compounds or commercially available antioxidants.

On-Demand-Type Device with Switchable Functions Responding to the Needs

Semiconductor devices, represented by transistors, are continuously improving at a rapid pace. However, there are darkening signs regarding their future development. To continue to improve the performance of electronic information devices, various new 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 is difficult to switch to 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 to the functions of integrated circuits when necessary.

On-demand-type device is fabricated using a stacked structure comprising a mixed conductor $\text{WO}_3$ 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 conductivities at the interface between the mixed conductor and the electrodes. We successfully realized diverse functions by utilizing these changes in conductivity properties, and also achieved switching of those functions.

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

References

Revealing the Anomalous Tensile Properties of WS$\textsubscript{2}$ Nanotubes by in situ Transmission Electron Microscopy

WS$\textsubscript{2}$ nanotubes consist of covalently bonded S-W-S coaxial shells which are weakly joined by their van der Waals interactions. The structure of carbon nanotubes (CNTs) and boron nitride nanotubes (BNNTs). Compared with the C and BN counterparts, WS$\textsubscript{2}$ nanotubes have a substantially different atomic structure, that is, each shell consists of three atomic layers rather than having a simple planar sp$^2$ structure. It is fundamentally interesting to have a comprehensive investigation on the structure dependent mechanical properties, and critically important to understand the tolerance of its memory and long-term memory, which plays a significant role in the mechanical properties for their practical applications.

In this work, we used an in situ transmission electron microscopy (TEM) method to investigate the tensile properties of the multilayered WS$\textsubscript{2}$ 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 “defect-free” manner, with its outer part broken and its inner part pulled out. However, there are two inner layers of WS$\textsubscript{2}$ nanotubes with almost “defect-free” structures. In addition, we observed that one of the WS$\textsubscript{2}$ nanotubes fractured in a “sword-in-sheath” manner, with its outer part broken and its inner part pulled out. However, as shown in Figure 1, the fracture of the WS$\textsubscript{2}$ nanotubes is due to the regarded “imperfections”, most of the present WS$\textsubscript{2}$ nanotubes fractured through multi-shell breakage rather than via a single-shell failure, which led to a much higher loading force than the thin WS$\textsubscript{2}$ nanotubes with almost “defect-free” structures studied previously.

References

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

Nafion® is a perfluorosulfonate ionomer (PFSI), which contains a fluorocarbon backbone with pendant side chains that terminate with a sulfonate group and the most commonly used in proton exchange membrane fuel cell (PEMFC) as membrane and ionomer. The hydrophilic properties of the fluorocarbon backbone and the hydrophobic properties of the highly ionic sulfonate side chains provide such unique structures. The hydrophilic domain of the PEMFC facilitates the uptake and transport of water and proton which shape affect at the performance of a PEMFC. Thus, understanding of the hydration behavior of Nafion 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 $\omega$ and $\omega'$ generate one photon of sum frequency $(\omega + \omega')$, 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 Nafion 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 shown that structure of water molecules at Nafion membrane surface will change from “ice-like” to “liquid-like” by increasing RH in bulk membrane. At Nafion 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-water interface selectively.

References