Events

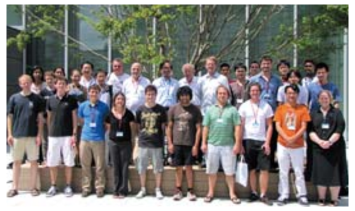
A Commemorative Ceremony for the Completion of NanoGREEN/WPI-MANA Building

On July 5, a commemorative ceremony for the completion of the new NanoGREEN/WPI-MANA building at Namiki site, NIMS, was held with over 150 attendees, including 116 guests. The ceremony began with an opening address by Dr. Sukekatsu Ushioda, NIMS President. Then four guests, Dr. Ken-ichi Ichihara (the Mayor of Tsukuba city), Mr. Koichi Morimoto (Deputy Director-General of the Research Promotion Bureau, MEXT), Dr. Teruo Kishi (Chair of Executive Board, Tsukuba Innovation Arena), and Prof. Toshio Kuroki (Director of WPI Program), made congratulatory speeches. They encouraged the researchers at MANA and expressed their great expectations that further promotion of fusion research will produce innovative results in various fields.

Participants in the Auditorium of the WPI-MANA building

The 8th MANA-Cambridge/UCL-UCLA Nanotechnology Summer School

The 8th MANA-Cambridge/UCL-UCLA Nanotechnology Students' Summer School was held at MANA, from August 27 to 31. The 19 participating students from MANA/NIMS, University of Cambridge, University College London, and UCLA were divided into three teams, where they became "agents" who should tackle the "Mission Impossible: Promoting ignorance, awareness, and crazy ideas" received from the instructors. The students spent much time for group work to execute the mission through active discussion and presented a mission report on the last day of the school.



Participants of the summer school

MANA 5th Anniversary Memorial Symposium

On October 3, MANA 5th Anniversary Memorial Symposium was held with a total of 257 attendees to commemorate the five years since MANA's inception.

The Symposium started with a welcome address by NIMS President Dr. Sukekatsu Ushioda and continued with three congratulatory speeches by Prof. Toshio Kuroki (WPI Program Director), Prof. Gunzi Saito (WPI Program Officer) and Prof. Sir Mark Welland (MANA Satellite PI at University of Cambridge).

Subsequently, MANA Director-General Dr. Masakazu Aono spoke about "Five-year journey and future challenges of MANA" and Prof. Yoshinori Tokura from University of Tokyo gave a special lecture entitled "Emergent electromagnetic phenomena in solids". The later part of the program was entitled "Our Future Challenge in MANA" and consisted of eight oral presentations by the MANA researchers.

The participants in the Auditorium of the WPI-MANA building

1st UdeM-MANA Workshop on Nano-Life

On July 19, MANA and the University of Montreal (UdeM) jointly held a workshop at UdeM.

The workshop aimed to promote cooperative research and exchange of researchers to execute the research on nano-life according to a MOU signed between both institutes last year. 9 oral presentations were performed by researchers from both institutes. Active discussions on the latest research results from the fields including nanotechnology and medical science were held by 32 participants.

Participants of the workshop

Awards

Received the Tsukuba Encouragement Prize

Dr. Yusuke Yamauchi

Dr. Yusuke Yamauchi, MANA Independent Scientist, received the Tsukuba Encouragement Prize from the Science and Technology Promotion Foundation of Ibaraki On July 25. The prize is awarded to young researchers living in Ibaraki Prefecture who have great potential for producing remarkable results in science and technology.

The prize was given to Dr. Yamauchi for his marked work on "Toward effective utilization for rare metals: Development of new nanoporous metals".

Visitor

Deputy Minister of the National Science Council, Taiwan, Visited MANA

Prof. Dr. Chung-Yuan MOU, Deputy Minister of the National Science Council, Taiwan, visited NIMS on September 5, 2012. Prof. Mou received a MANA overview presentation by Mr. Takahiro Fujita, MANA Administrative Director, and had a tour of laboratories in the WPI-MANA building. Prof. Mou is an expert of nano-materials science, in particular biomedical applications. He was actively involved in discussions with researchers at MANA.

Prof. Chung-Yuan Mou (center)

Newly Appointed Researchers

◆MANA Scientist◆

Dr. Lok Lumar Threstha

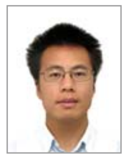
◆Independent Scientist◆

Dr. Ryoma Hayakawa

Dr. Joel Henzie

◆ICYS-MANA Researchers◆

Dr. Shinsuke Ishihara



Dr. Daiming Tang

CONVERGENCE No. 12, Eng. Ed., issued on October, 2012

Outreach Team
International Center for Materials Nanoarchitectonics (MANA)
c/o National Institute for Materials Science (NIMS)
1-1 Namiki, Tsukuba, Ibaraki, 305-0044 Japan

Phone: +81-29-860-4710
Facsimile: +81-29-860-4706
Email: mana-pr@ml.nims.go.jp
URL: http://www.nims.go.jp/mana/

"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.

wpi
International Center for Materials Nanoarchitectonics (MANA)
No.12
Oct. 2012

CONVERGENCE

Researchers at the Forefront of Safeguarding the Earth and Society
— Kazuhito HASHIMOTO

There is No Room at the Bottom
— James K. Gimzewski

Outreach Activities to Increase Public Interest

MANA's Research Outcome

17β-Estradiol Polysaccharide Conjugates for Cardiovascular Therapies
— Françoise M. Winnik

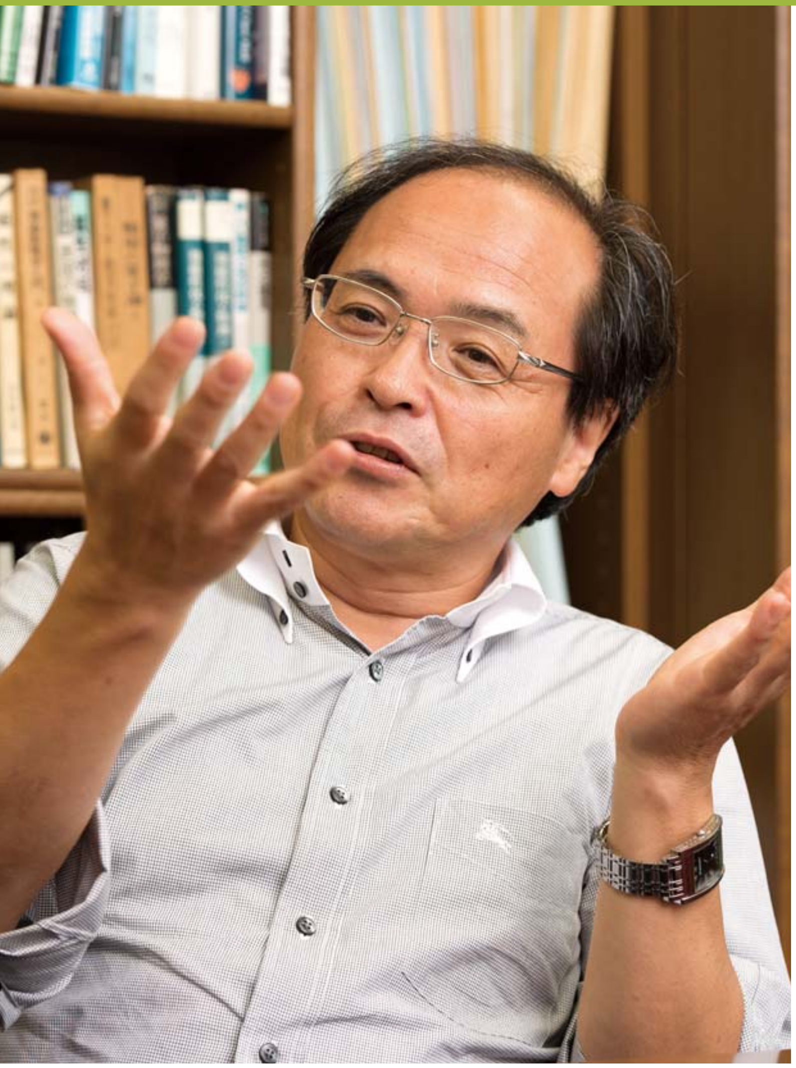
Atomic-Scale Design of Novel Nanomaterials for Fuel Cell Electrodes
— Satoshi TOMINAKA

Toward the realization of artificial photosynthesis:
Carbon Dioxide Reduction and Fuel Production by Oxide Photocatalysts
— Jinhua YE

Oxygen Diffusion in Perovskite Oxides
— Ken WATANABE

Researchers at the Forefront of Safeguarding the Earth and Society

Interviewew: Akio ETORI, Science Journalist



Kazuhito HASHIMOTO

After graduating from the Graduate School of Science, University of Tokyo (UT) in 1980, Mr. Hashimoto (D.Sc.) gained the appointments of being a technical associate and then a research associate at the Institute for Molecular Science, UT. He then obtained a position as a lecturer at the Department of Applied Chemistry, School of Engineering, UT in 1989 before promoting to an associate professor in 1991. Dr. Hashimoto became a full professor at the Research Center for Advanced Science and Technology, UT in 1997, and then served as the director from 2004 to 2007. He has been a professor at the Department of Applied Chemistry, UT since 2007. Dr. Hashimoto has been actively involved as the principal investigator in a variety of interdisciplinary projects that include: Photofunctionalized Material Project sponsored by Kanagawa Academy of Science and Technology (1993–1999); ERATO Light Energy Conversion Project of the Japan Science and Technology Agency (2007–2012); NEDO's Project to Create Photocatalyst Industry for Recycling-oriented Society (2007–2012); and NEDO Microbial Catalyst-based Power Generation Wastewater Treatment Project (2012–). His interests revolve around the design, creation, and industrial use of new photofunctionalized materials, and cover a wide range of areas from semiconductor photocatalysis, organic thin-film solar cells, molecular-based magnetic materials, and microbial electrochemistry. Dr. Hashimoto has been awarded a number of prizes that include the following: IBM Japan Science Prize (1997); Prime Minister's Award (for industry-academia-government collaboration), Nikkei Earth Environmental Technical Prize (2004); Imperial Invention Prize, Yamazaki-Teiichi Prize (2006); and Chemical Society of Japan Award (2012). He is currently a member of the Science Council of Japan, METI Industrial Structure Council, MEXT Council for Science and Technology, and MANA Evaluation Committee.

Strongly Motivated to Make a Social Contribution

—NIMS, the host institute of MANA, has the motto that "The Value of Materials is in Their Use." What are your priorities with materials research?

There is no doubt that usefulness is one of the key points. However, there are a number of obstacles to overcome before new materials reach practical application, something I learned while researching photocatalysts. Its cost effectiveness is the first test the industrial use of a novel material has to pass, and even if the basic research on it has been completed. Safety and legal issues can also exist that have to be cleared. In addition, if a new material is expected to replace a current one the marketing strategies of the manufacturer of it can also influence the applicability of a new material. Manufacturers thus have to adapt to changing social demands. These are just some of the impediments that can prevent the practical use of the results of research. Materials scientists can often be too focused on 'producing' a novel material. Many researchers consider that their part in the process to be over once they handed the baton to others by thinking that "I have created such an excellent material that someone will find a way of using it." But in fact they still have a number of roles to fulfill. The researcher who has developed a material knows the most about it, and has the strongest motivation to make it eligible to be of social benefit. The researcher concerned therefore needs to be running alongside the other experts rather than merely handing the baton over. There is no end to the research involved with useful materials.

—How can you help young researchers to develop that type of mindset?

This may sound slightly overstated but I would like to stress the importance of recognizing the 'sense of crisis' we face with our current situation, and the differences between the 20th and 21st centuries. Our globe has been rapidly changing in the past 100 years. I would like young researchers to be more aware of the changes that have taken place in the direction of scientific research and the role which scientists need to fill in today's world. In the 20th century people simply could believe that development in science and technology would lead to greater happiness for mankind, and that society and the economy would maintain steady growth. It was an era when individual efforts contributed to the overall social welfare of people. The 21st century, however, has a completely different outlook. People no longer naively believe that development in science and technology leads to greater happiness, no matter how much convenience technological innovations provide us with. We are gradually recognizing that our overall socioeconomic system is becoming *saturated* and even *declining*, and we live in a society where individual efforts do not increase our overall welfare. Japan is at the forefront of those socioeconomic changes. We could indeed suddenly find ourselves lagging far behind the world's other leading nations.

I would hope that brilliant scientists, who are on the fast track to success, would have the guts to be the pioneering innovators of a new society and thus help dissipate the looming anxiety we have about our future. I particularly request the young scientists at MANA to be aware of being a part of an 'elite' group of scientists. The elite should not sit back and take advantage of other people's work; they are a group of leaders that can point out new directions, and therefore need to put in twice as much effort as everyone else. This age can be seen a challenge to the true capabilities of elite scientists.

Research that Promotes Symbiosis with Nature

—What are important points when selecting research themes?

Needless to say fundamental topics that stimulate our intellectual curiosity such as 'What is at the end of the universe?' or 'What was the origin of life?' are important for us to study. At the same time, however, topics directly related to human and social welfare are also very important, and for example the development of new energy sources, cancer treatment, and economic stability.

In past ages artists and scientists had patrons that supported their activities in the area of their patron's interest. They were presumably lucky to have found a patron that understood and had an interest in the work they engaged in. However, that said, they were probably abandoned once what they produced no longer interested their patron, I assume. Nowadays the public is the patron of researchers like us. Will people be interested in academic work that merely investigates certain physical properties of a material? Can that research convince the public of the need for it? Researchers involved in publicly-funded projects have the duty of explaining the potential use of the materials their research is involved with and also how their work can promote human wisdom, even if their research is unlikely to produce any tangible technological results. In other words, the social system cannot tolerate any research activities that are unrelated to social needs or basic human concerns. The public has assigned us to do research for them and therefore we must be fully aware of our role of making a social contribution.

—That awareness seems to be the basis of your research projects?

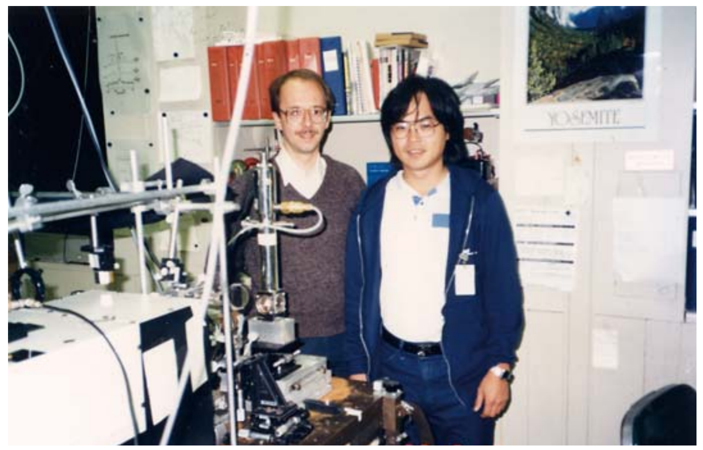
It is at least constantly on my mind, although I would hesitate to claim that my research has always fulfilled that. Over the last 5 to 6 years our laboratory has been researching new energy systems that utilize living organisms. The mainline research orientation of the 20th century was efficiency, and had turned away from nature. We now believe, however, that science and technology in the 21st century should move in the opposite direction; we must learn from and draw closer to nature and use or at least mimic natural mechanisms.

For example, common solar batteries convert about 15% of incoming solar energy, with the most excellent laboratory cells at present having a conversion efficiency of 43%. Plant photosynthesis, on the other hand, only converts 0.2% to 1% of solar energy. We have thus developed a system that is far more efficient than that of nature. Yet, I do not consider silicon solar cells to be outperforming plants. What are the differences?--this question triggered our study. The answer is quite straightforward. Plants proliferate in an appropriate environment, and heal themselves when damaged, whereas silicon solar cells cannot multiply by themselves. I have recognized that the essence of life is *auto-proliferation* and *self-restoration* rather than efficiency. This then made me want to create self-proliferating solar cells. Upon sharing that idea with my laboratory staff members they thought I was merely joking. However, the work we did after that demonstrated that lakes and paddies could serve as photo-electricity conversion systems via the combined use of photosynthetic microorganisms, rice plants, and electricity-producing bacteria, although the current photo-conversion rate is only 0.01% to 0.1%.

—It is important to learn from nature rather than just pursue more efficiency.

Correct. A lot of effort is being put into developing a highly efficient artificial photosynthesis system by extracting the essential features of charge separation functions from plants. I believe that 21st-century methodologies need to include the approach of achieving natural symbiosis by modeling natural phenomena, even if their energy efficiency can apparently seem rather low.

Materials at the Basis of Japanese Manufacturing Industries: Unique ideas involving nanotechnology and materials research



Dr. Hashimoto during a short-term stay at Bell Laboratories, Murray Hill, NJ, USA (1987).

—Five years have passed since MANA was approved as International Center for Material Nanoarchitectonics within MEXT's WPI Program. What do you expect from MANA as one of the MANA Evaluation Committee members?

Great advances have been made in the field of nanotechnology over the last 10 years. MANA has made significant contributions to its development, and particularly in the area of basic research. MANA's value will be highly appreciated if it continues to adapt any research findings to fulfilling social needs. NIMS is an incorporated administrative agency whose mission in turning basic research results into practical application for the good of the society. And in this regard it is very meaningful that MANA is located within NIMS. Materials form the basis of Japanese manufacturing industries. My expectation is that MANA, a center of excellence located within NIMS, will be a source of power that energizes the merits of Japan's technology.

I notice that many young MANA researchers speak fluent English, which is partly because English is the common language used at MANA where researchers from all around the world get together. I highly appreciate that researchers have such powerful language skills that enable them to make presentations and hold discussions in English. However, I am concerned that many young researchers seem satisfied with merely reporting that they created an interesting material like this or discovered new physical properties like that. They appear to think that the creation and investigation of physical properties of new materials are all that are needed in creative research. But no, there is much more to it. A high level of creativity is also required in changing a new material into something that has value and is needed by society, as I mentioned previously. I wish to encourage young researchers to tackle that challenge.

Research facilities that produce high-quality academic output and make a significant social contribution will attract and nurture enthusiastic scientists. I hope that MANA continues to be that kind of attractive place.

There is No Room at the Bottom

James K. Gimzewski
MANA Satellite Principal Investigator,
Nano-Materials Field
UCLA

There is no room for doing incremental research in today's world. Some 20-30 years ago there were relatively few scientists and it was an elitist community. Today we have too many young scientists. The education system has produced a glut of specialists with a narrow focus also in their later research. However, the basis of that system is antiquated being based on 19th century values which were appropriate for the industrial revolution and where knowledge was stored in libraries accessible to a few. Today's world is one of cheap human-wave work forces as China aggressively expands and exports products on the international marketplace in its seemingly never ending quest to dominate global consumer markets. Additionally, in the USA, Japan and Germany robots, computers and advanced communication systems have replaced the majority of blue and white-collar jobs while their companies ship many operations and activities overseas. This trend will continue rendering our societies in a new territory where the inequality of rich and poor will expand even further and unemployment will continuously increase.

In history over the past three centuries humankind has experienced revolutions driven by one essential thing: the innovative capabilities of the human mind. Innovation created the industrial, chemical, electrical and information-technology-communication, and some may say social, revolutions. There are, what some have termed, singularities in the timeline of technology advancement evidenced by inspecting a graph of GDP growth with time. While one may be tempted to ascribe a specific invention, such as the computer or printing press, to the two singularities characterized by a dramatic change in slope around 1700 and again around 1950, it has been argued and quite convincingly that the mass availability of new communications systems (books and computers) enabled humans to innovate diverse ranges of new products and so create a criticality in their society. The washing machine, the Walkman and so on result from emergent critically originating from Nikola Tesla genius innovations to transport and use electricity for useful tasks.

We need therefore to create new, not incremental, innovation that may create a societal and technology driven revolution. That to me is the underlying core of the MANA grand challenge. Innovation means top thinking and top working using creativity to its highest potential. There is no room at the bottom, none, for mediocre incremental research. Publishing another paper on some boring dry dead subject is the bottom. There is no room at the bottom in MANA but there is plenty of room at the bottom on the street.

There is a lot of room for mistakes along the path. Only through mistakes can innovation occur. Learning is through mistakes. This is essentially how the mind works and creates. Without mistakes mental stagnation sets in. Another essential ingredient of innovation is to aim high and to pick a challenge that may seem impossible at the time. Aim for the sky and take a risk. One can only take on such a challenge with a strong heart as well as a strong mind. A samurai spirit is needed and a sword that can cut through obstacles on the way. It's necessary to destroy old thoughts and ways on the path to innovation. Without change and breaking established paths can new ideas succeed in being realized.

The final and underlying pillar of innovation is absolute unrelenting intent and determination but tempered with a sensitivity and nimbleness to adapt to the developing environment. The plasticity of the mind and its ability to adapt to its surroundings is an essential trait of intelligence.

I am known for my work on the scanning tunneling microscope yet I have taken on a very different challenge. I want to create a machine that thinks, a machine that possess physical intelligence. I want to create a synthetic brain. Such a system does not exist and promises to cause a revolution one might call the post-human revolution. Such a machine cannot be created with the von Neuman architecture of CMOS. There is some evidence that emergent intelligence is occurring within the highly interconnected world wide web of social networks and that power law avalanches such as the Arab spring and stochastic behavior such as the non gaussian flash crash of the trading markets are inevitable consequences of slow driving in any highly interconnected network. MRI studies of the human brain also show similar behavior in their dynamics. Together with Aono-san we decided that the atom switch is the basis of an intelligent machine. In this 'atomic brain', the neuromorphic characteristics of long and short-term memories have already been demonstrated. The next step is underway by using random networks of some billion synthetic synapses per square centimeter. We have discovered such systems exhibit power law dynamics, self-organized criticality, recurrent dynamics and memories.

Such a system has a resemblance to Alan Turing's proposed unorganized machine also comprised of random interconnections of NAND gates. Yet in our experimental embodiments we have discovered the existence of self-organized dynamics. Such a machine has the capacity to sense a great number of inputs simultaneously from thousands of nanosensors and to react through robotics using locomotion in real-time. Essentially the machine can learn to self-replicate and as such change the relationship between man and machine such that the boundaries are unclear. This development will change the world and the socio-economic balance of Japan if it leads in the collaborative research as it does presently. It can create a new synthetic workforce that will exceed even the giants of manufacturing and will pose new questions for humans in a post human world. This is the grand challenge and it will be achieved within the next decade. Intelligent robots with senses exceeding ours endowed with a capacity to think that may well exceed the vast majority of the world's people.

James K. Gimzewski

James K. Gimzewski FRS, is an internationally acclaimed researcher in the field of Scanned Probe Microscopy, Nanoarchitectonic Systems, Nanoelectronics and Nanomechanics. He joined IBM Zurich Labs in1983 and since 2001 is a Distinguished Professor of Chemistry at UCLA, Core Director at CNSI and Satellite co-Director and PI at MANA-NIMS.

Outreach Activities to Increase Public Interest

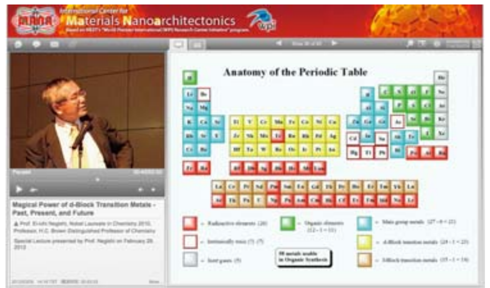
Achieving wider recognition of the results of excellent research necessitates the appropriate information being provided to both the public and other experts. MANA is actively involved in various outreach programs in both the Japanese and English languages that include experts in materials science and other researchers, as well as the general public, including elementary school right through to college students. Websites, as well as paper based and other media are used to disseminate information, while events and seminars are held to promote interactive discussions. Below are some of MANA's recent activities.

■ Web-based Information Resources

MANA's latest research findings are reported in a timely manner via the on-line "MANA Research Highlight" series that aims at providing information on materials science to experts throughout the world. Volume 3 of the on-line series, which was released on July 26th, 2012, highlighted "Bone tissue engineering: Attaching proteins for better regeneration."

In addition, some guest speakers' presentations made at MANA International Symposium are also made accessible on-line via use of a special web streaming technique that simultaneously displays both a video of the speaker and the slides that their presentation involve.

MANA Research Highlight, Vol. 3.

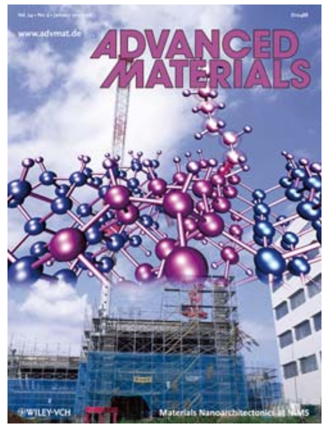


Video stream of an invitational speaker at MANA International Symposium 2012.

■ Publication Activities

MANA was the first Japanese research institution to feature in a special issue of *Advanced Materials*, which was published on January 5th, 2012. *Advanced Materials* is one of the leading peer-reviewed journals that specialize in materials science. MANA also featured in an August 2011 special on-line issue of the international materials science journal, *Science and Technology of Advanced Materials*.

Moreover, MANA publications that aim at lay people include the picture book *Nima's Adventure* and the cartoon *The Challenging Daily Life*, both of which have earned very positive reputations.



Special issue of the Advanced Materials journal.

Picture book: Nima's Adventure.

Cartoon: The Challenging Daily Life.

■ Educational Events

MANA organizes a variety of educational events for junior and senior high school students that involve nanotechnology and materials science.

Idea Contest "Challengers for the Future"

Jointly sponsoring the event with the WPI-Advanced Institute for Materials Research (WPI-AIMR) MANA launched an idea contest for young students, in which the participants make suggestions on the possibilities of materials science.

Idea contest awards ceremony.

Summer Science Camp

As part of the Summer Science Camp 2012, which was sponsored by the Japan Science and Technology Agency, MANA received 10 high school students chosen from across the country, who joined a 3-day program to enjoy hands-on experience with cutting-edge nanotech developments.

Participants putting into practice nano-imprint lithography.

WPI Research Center Joint Symposium

A series of WPI Research Center Joint Symposia, which first commenced in 2011, provide a wonderful opportunity for junior and senior high school students to directly interact with front-line scientists. This year MANA will host the symposium on November 24 in Tsukuba, Ibaraki.

MANA booth at 2011 Joint Symposium.

Other activities include: a workshop at Science Agora 2010; Science Café "Melting Pot Club"; lectures by Nobel Prize laureates; a booth presentation at the Science and Technology Festa held in Kyoto; a joint presentation by the six WPI research centers at the 2012 AAAS Annual Meeting held in Vancouver; and MANA International Symposium.

MANA aims to promote public interest in scientific research through the abovementioned outreach programs.

17β-Estradiol Polysaccharide Conjugates for Cardiovascular Therapies

Françoise M. Winnik
MANA Principal Investigator
Nano-Life Field
University of Montreal

The steroidal hormone 17β-estradiol (E2) has been studied extensively in the context of cardiovascular therapy, ever since it was reported to exert beneficial effects in the prevention and treatment of cardiovascular diseases. The foremost role of E2 is to regulate sex-related processes via estrogen receptors (ER) located in the cell nucleus. This genomic action of E2 takes place over periods of a few hours to a few days. The effects of E2 in cardiovascular processes are believed to occur much faster and to be mediated by a small population of ERs located in the cell membrane, not in the nucleus (Figure A). For maximum cardiovascular beneficial effects, E2 must be able to interact with membrane-associated ERs without activating nucleus ERs. To achieve this goal, E2 was conjugated to chitosan phosphorylcholine (CH-PC), a non-toxic water-soluble membrane-mimetic biopolymer,[1,2] known to support the growth of various cell lines, including endothelial progenitor cells.[3]

Thin films of CH-PC-E2 (Figure B) were prepared by spin casting aqueous CH-PC-E2 solutions on a hydrophilic silicon wafer. Angle-resolved XPS analysis of the dried films revealed a significant E2 enrichment of the topmost section of the film, attributed to the preferential migration of E2 towards the film/air interface upon drying (Figure C). To probe the location of E2 in CH-PC-E2 films exposed to aqueous media, films spin-coated on quartz crystals were rehydrated with a phosphate buffer saline (PBS) in the sample compartment of a quartz crystal microbalance with dissipation (QCM-D (Figure D). The QCM-D signals recorded upon injection of ER-α solutions (10 to 100 nmol) and flushing with buffer indicated that ER was adsorbed permanently on CH-PC-E2 films. Overall, this study provides strong evidence that CH-PC-E2 conjugates are able to activate specifically non-genomic E2 pathways and are promising candidates for use in cardiovascular therapies.

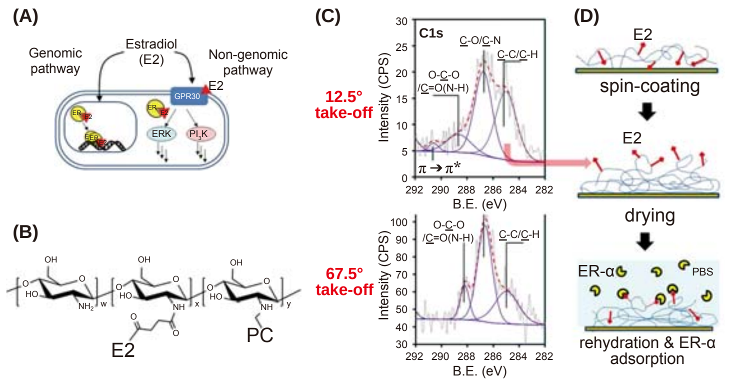


Figure (A) Representation of genomic and non-genomic estrogen pathways.
(B) Structure of chitosan phosphorylcholine E2 conjugates
(C) Narrow XPS scans and deconvolution of the C1s peak of a spin-coated CH-PC-E2 film.
(D) Preparation of CH-PC-E2 films and their interactions with ER-α.

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Toward the Realization of Artificial Photosynthesis:
Carbon Dioxide Reduction and Fuel Production by Oxide Photocatalysts

Jinhua YE
MANA Principal Investigator
Nano-Power Field

Artificial photosynthesis, or the solar-powered process of producing oxygen and hydrocarbon fuels from water and carbon dioxide, could be the ultimate technological solution to the resource and environmental problems modern society faces, for example the energy shortage and global warming. Development of this new technology is part of WPI-MANA's three grand challenges.

We have been involved in researching novel semiconductor photocatalyst materials, as well as carbon dioxide photoreduction and fuel production using those materials. We discovered that in addition to the design and development of materials of sufficiently negative conduction band potential, control of surface characteristics as well as micro- and mesoporous structures play an important role in controlling multi-electron reactions in thereby promoting product selectivity and improving carbon dioxide adsorption properties. Some of our recent studies have revealed controlling the oxide surface oxygen deficiency to be critical in carbon dioxide reduction reactions,[1,2] and which is briefly outlined below.

$SrTiO_3$, synthesized in a solid-phase reaction, was heated in an argon atmosphere at 1200 to 1400°C in deliberately introducing oxygen vacancy.[1] Various $SrTiO_{3-\delta}$ compounds with different levels of oxygen deficiency were used in carbon dioxide reduction reactions under visible light radiation. The samples heated at 1300°C yielded the largest amounts of methane. The different levels of catalytic activity presumably resulted from oxygen deficiency-related synergistic effects on the visible light absorption and the carbon dioxide adsorption properties of the catalyst surface. In addition, theoretical calculations suggested the observed increase in visible light absorption to be attributable to excitation of the conduction band from new bands being created by the oxygen deficiency and which does not reduce the conduction band, i.e., the reduction potential of $SrTiO_{3-\delta}$.

Similar findings were also observed with WO_3 nanowires.[2] In this case, ultrathin (diameter < 1 nm) oxygen-deficient $W_{18}O_{49}$ nanowires, produced via solution-phase synthesis, were treated with H_2O_2 in thereby deliberately controlling the surface oxygen deficiency levels. The nanomaterials then being used in carbon dioxide photoreduction resulted in the eight electron reaction product methane being obtained in amounts that increased with the degree of oxygen deficiency.

In conclusion, our research clearly demonstrated controlling the level of oxygen deficiency of the oxide catalyst surface to be critical in effective photoreduction of carbon dioxide and hydrocarbon fuel production, and thus warrants further research in thereby elucidating the reaction mechanisms and developing highly efficient catalysts.

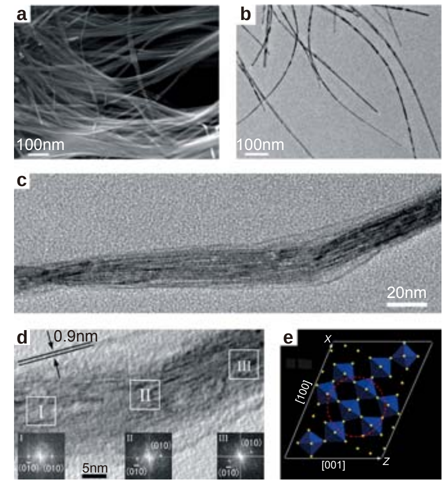

Figure 1. (a, b, c) SEM, TEM, and high-magnification TEM images of the $W_{18}O_{49}$ nanowires. (d) HRTEM image of the ultrathin nanowires. (e) Scheme: the cross section of a 0.9 nm nanowire inside one $W_{18}O_{49}$ unit cell oriented along the [010] direction.

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Atomic-Scale Design of Novel Nanomaterials for Fuel Cell Electrodes

Satoshi TOMINAKA
MANA Independent Scientist

Fuel cells are one of the important power sources for reducing carbon dioxide emissions, and in order to diffuse them widely highly-functional electrode materials need to be developed. Since their requisite properties are tough such as catalyst activity, large specific surface area, chemical and electrochemical stability, conductivity, and low cost, many researches have been conducted all over the world.

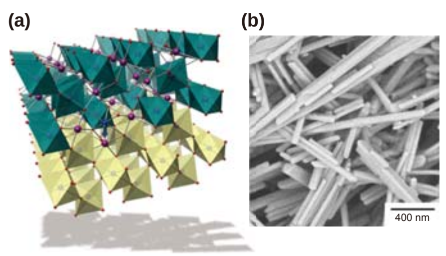
I have designed electrode materials at atomic scale, taking into consideration phenomena occurring at a different scale from atomic to micron scale. Moreover, by assembling the materials rationally, innovative devices and systems are also developed.

Herein, I introduce recent achievements on nanostructured electrode materials of titanium oxides, which are expected to be applicable not only to fuel cells but also to electrolytic industries. Titanium oxides are chemically stable, and some of their reduced phases exhibit high electric conductivity. These properties have placed reduced titanium oxides as promising alternative to carbon materials, which are not stable in fuel cell working conditions, but their surface area was not enough.

Recently, our research group succeeded in the synthesis of nanostructured reduced titanium oxides via a low-temperature reduction approach. The materials thus obtained for the first time exhibited metallic conduction, though the crystal structure was determined to be corundum, which was known to be semiconductor. Through detailed electron microscope analyses, atomic diffusion inside materials was found to be important for such conversion to metallic ones (Figure a).

The method can convert nanostructured TiO_2, which have been synthesized by many groups, into highly functionalized materials with morphology retention, thus we believe that our approach is versatile and will be applied widely. For example, rod-shaped nanostructured TiO_2 was also successfully converted into reduced one (Figure b). Furthermore, the material was proved to work as a stable electrode in acidic solution (Figure c). These results strongly indicate their application as electrode materials alternative to precious metals.

For the applications as electrocatalysts, further research works are under investigation. Also, in order to acquire better understanding of conduction mechanism, detailed analyses on atomic structure and electronic structure will be reported soon.



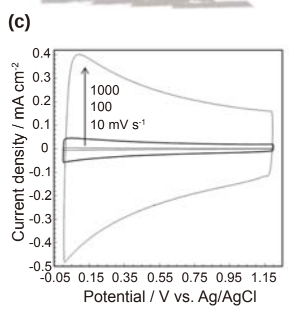


Figure (a) Low-temperature reduction from TiO_2 to reduced, corundum phase. (b) SEM image of reduced rod-shape nanostructures. (c) Electrochemical response in acidic solution.

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Oxygen Diffusion in Perovskite Oxides

Ken WATANABE
ICYS-MANA Researcher

Perovskite oxides exhibit many kinds of electric property such as insulator, semiconductor, ioni conductor and mixed conductor (electron and ion). Due to its property, perovskite has been widely used as solid oxide fuel cell, photocatalyst, electroceramics and so on. In order to control such electric property of the perovskite oxides, the oxygen defect is one of the important factors. In this study, I focus on the oxygen tracer diffusion in perovskite oxides with an isotopic ^{18}O (mass number = 18), to evaluate the oxygen defect in a solid. When the solid is annealed in $^{18}O_2$ atmosphere, surface exchange reaction will be occurred between ^{18}O and ^{16}O in gaseous phase and solid, respectively. As the result, ^{18}O will diffuse into inside of the solid. From those diffusion data, we can discuss about the oxygen defect in solid, because the oxygen diffusion in perovskite oxide can be attributed to an oxygen vacancy migration.

Here, I'd like to show you the result of the oxygen diffusion behavior in $BaTiO_3$. Figure 1 shows the cross-sectional ^{18}O concentration map of the reduced $BaTiO_3$ ceramics after annealing in $^{18}O_2$. The ^{18}O concentration in the grains was almost constant. On the other hand, the ^{18}O concentration was drastically decreased around the grain boundary. Therefore, it was found that the grain boundary of the reduced $BaTiO_3$ acts as a blocking layer against the oxygen diffusion. In general, it is well known that "the grain boundary acts as the fast diffusion path for mass transportation", because of its disordered structure. However, the obtained finding in this study is precisely opposite result. In addition, it was found that the blocking behavior strongly depends on the diffusion temperature, reduction treatment. Furthermore, any impurity phase around the grain boundary was not observed from the elemental map obtained by SIMS. Thus, it seems that the formation of the blocking layer is related to be the local defect structure around grain boundary and we need to reveal relationship between the local defect structure and its function, in order to discover a new function of the material.

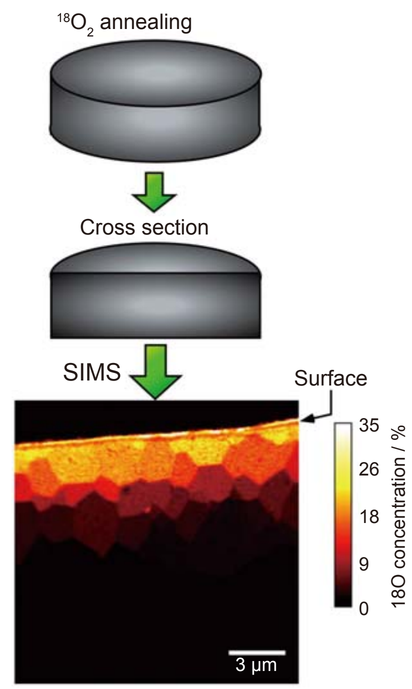

Figure 1. Cross-sectional ^{18}O concentration map of $BaTiO_3$ ceramics by SIMS

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