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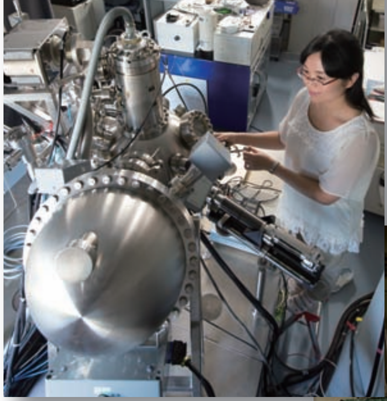
Impact of NIMS Research Results on Society, 2013



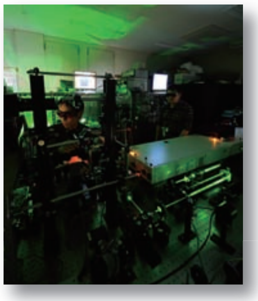
Impact of NIMS Research Results on Society, 2013

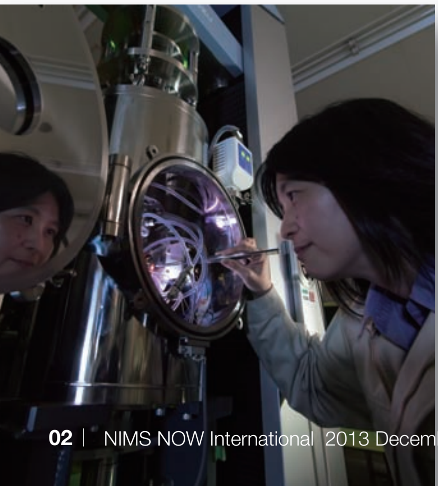
There are a number of ways we can deliver research results to society.
For example, we can present articles to academic circles, or make presentations at various events.

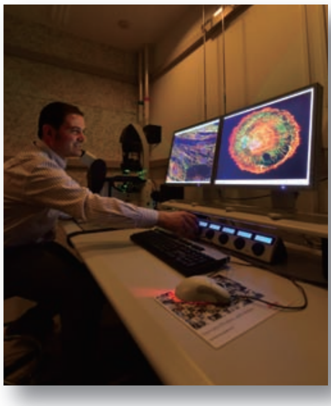
Among them, we consider presenting research results through mass media as press releases to be an important means that is capable of delivering the results to a much wider audience.

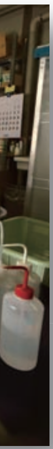
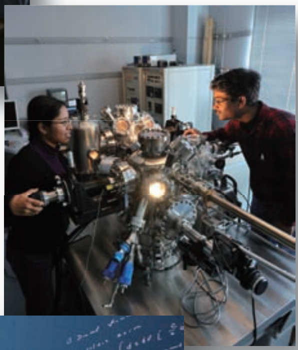
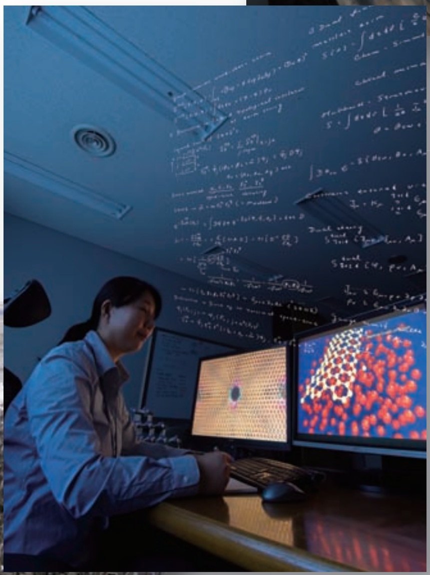
When a breakthrough is found in basic research, when many years of steady research finally produce a result, or when a research result is commercialized as a product, the result is presented through a press release.
Press releases can be regarded as an aggregation of NIMS' research.

This issue selects research results announced in press releases during 2013 which received particularly strong responses, and introduces them together with our interviews with the researchers.
It is expected that they will give you insights into where NIMS has most recently been heading.







NIMS Press releases 2013

- Success in Fabrication of One Dimensional Organic Molecule Chain
- Success in Theoretical Design of Photocatalyst Enabling Mass Production of Hydrogen
- Fullerene Crystals with Bimodal Pore Architectures
- Development of High Sensitivity Detection Method for Diluted Ionic Mercury in Water
- First Success in Real Time Observation of Process of Solubilization of CNT by Polymer
- Novel Drug Delivery System Releases Drugs in Response to Compression by the Patient's Hand
- Success in Observation of Swelling of Single-Particle of Silicon Electrode for Lithium Ion Batteries during Charging Reaction
- Discovery of New Gigantic Swelling Phenomenon of Layered Crystal Driven by Water
- 2D Organic Materials: World's First Synthesis of Thiophene Nanosheets with 3.5nm Thickness
- Development of Coating Method that Accelerates Bonding with Bone by 3 Times
- Publication of NIMS Creep Data Sheets, Space Use Materials Data Sheets, and Structural Materials Data Sheets
- Formation of Functionalized Nanowires by Control of Self-Assembly Using Multiple Modified Amyloid Peptides
- Observation of skyrmions (magnetic vortex structures) in a ferromagnet with centrosymmetry
- Novel Synthesis Technique for High Efficiency Conversion of Source Gas to Diamond
- Development of Nonvolatile Liquid Anthracenes for Facile Full-Colour Luminescence Tuning
- Smart Anticancer "Nanofiber Mesh"
- Clarification of Dynamical Process of Aluminum Surface Oxidation
- Elucidation of Spin State of Conduction Electrons in Graphene
- Theoretical Study Revealing Possibility of A Quantum Material To Transport Zero-Resistance Current Above Room Temperature
- Development of Hydrogel Enabling Repeated Postmodulation in Controlled Spatial Domains by Only UV Irradiation
- Success in Development of Novel Chirality Sensing Technique Enabling Easy Determination of Optical Purity
- First Successful Development of High Performance Reversible Electrode Catalyst for Next-Generation Metal-Air Secondary Batteries
- Entanglement from Triangular Dots
- Success in Elucidating Reduction Reaction Mechanisms of Lithium-Ion Battery Electrolytes, Using the K Computer
- Controlling the Size and Helicity of an Electron Magnetic vortex "Skyrmion"
- World's First Success in *In Situ* Tracking of Electrochemical Reactions at Solid/Liquid Interfaces by Photoelectron Spectroscopy
- Success in Developing an Oxide Semiconductor with a New Elemental Composition Having the Property of Stability
- Discovery of Ferroelectric Structural Phase Transition in a Metal Substance That Was Predicted to Be Theoretically Possible About a Half Century Ago
- Dye Absorption Structure of Dye-Sensitized Solar Cells Elucidated on Molecular Level
- Development of High-Performance Oil Absorbent for Resources Development
- Orientation-controlled crystalline thin film of perovskite oxide successfully grown on a glass substrate
- Success in Fabrication of Three-dimensional Structure of Single-Element Quasicrystal
- Carbon dioxide "breathing phenomenon" found in clay minerals
- Successful Demonstration of the Principle for Increasing the Efficiency of Solar Cells Using an InGaN Multilevel Inter Mediate Band
- World's First Success in Making Graphene Products with Strutted 3D Structure
- *In Situ* Band-gap Tuning of Graphene Oxide

＊ The press releases announcing research results are all accessible on the NIMS website.
http://www.nims.go.jp/eng/news/press/

PRESS RELEASE

Success in Theory-Driven Development of Photocatalyst

—Expected to Accelerate Technologies for Producing Hydrogen from Water using Solar Light—

Senior Researcher,
Environmental Remediation Materials Unit
Naoto Umezawa

Unit Director,
Environmental Remediation Materials Unit
Jinhua Ye

Using computer simulated experiments for materials search

Photocatalysts,[1] as represented by titanium oxide, are widely applied to products with environmental cleanup effects, such as antifouling or antibacterial effects. However, the water photolysis reactions achieved to date have not been strong enough to produce a large amount of hydrogen, which is a next-generation energy source. Because the development of photocatalysts had conventionally been carried out based on the intuitions of researchers without clear design guidelines, systematic improvement of photocatalytic activity was difficult. Therefore, attempts have been made in recent years to reduce the burden of materials search by identifying promising materials in advance through simulated experiments using computers. In this research, we succeeded in the theoretical design of photocatalysts that exhibit high water-splitting activity under visible light irradiation.

Utilizing theory, what should strontium titanate be doped with?

Strontium titanate ($SrTiO_3$) is expected to serve as a photocatalyst that enables the production of hydrogen solely using sunlight, due to its high stability under light irradiation and its strong photoreduction ability. Nevertheless, since its optical absorption edge is located in the ultraviolet region, it cannot effectively use visible light, which constitutes the most part of sunlight. Thus, research has been conducted to adjust the absorption edge into the visible light region by doping[2] $SrTiO_3$ with transition metals[3] such as chromium (Cr). In recent years, much research has been done on co-doping of transition metal elements and other elements with the aim of further enhancing the photocatalytic activity.

Cr-doped $SrTiO_3$ has been known to exhibit high hydrogen generation efficiency when Cr is trivalent (Cr^{3+}). This is because when Cr is tetravalent (Cr^{4+}), the photocatalytic reaction is inhibited due to electron capture (Fig. 1). Therefore, in this research, we attempted to stabilize Cr^{3+} by raising the Fermi level[4] through doping Cr together with various other elements. By using calculation based on the density functional theory,[5] we estimated the position of the Fermi level for the case where the Sr in $SrTiO_3$ is replaced with La or Y, Ti is replaced with Ta, Sb or Nb, and O is replaced with F, with the condition of charge neutrality, and we studied which dopant enhances the photocatalytic activity the most when co-doped with Cr. As a result, we predicted a substantial rise in the Fermi level and a high Cr^{3+} concentration when La, which has the capacity to form conduction electrons in $SrTiO_3$, is co-doped with Cr (Fig. 2a).

Our experiments confirmed that $SrTiO_3$ co-doped with La and Cr exhibits higher hydrogen generation efficiency under visible light irradiation than that co-doped with other elements, thus demonstrating the validity of the theoretical prediction (Fig. 2b).

1) Photocatalyst: A material that exhibits catalytic action when irradiated with light. In this research, water is split by using the catalytic action obtained through irradiation with visible light, which is dominant in sunlight.
2) Doping/co-doping: Manipulation whereby an element in the lattice of a host material ($SrTiO_3$ in this research) is replaced with another element (dopant; Cr or La in this research) given from outside. Doping that replaces two kinds of elements is called co-doping.
3) Transition metal: Collective term for the elements in groups 3 to 11 on the periodic table.
4) Fermi level: Energy level at which the probability of electron occupancy is one half. In the case of a semiconductor like $SrTiO_3$, the Fermi level lies within the forbidden band where no energy level exists, and its position can be controlled by doping it with different kinds of elements.
5) Density functional theory: A rigorous theory guaranteeing that total energies of electronic systems of molecules and solids can be calculated based on electron density. Some approximations must be applied to practical calculations.

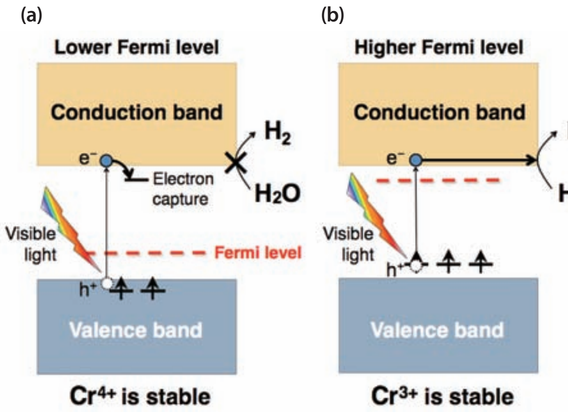


Fig. 1 Effect of the position of the Fermi level on the oxidation number of Cr and the photocatalytic activity.
(a) When the Fermi level is low, the activity is reduced because unoccupied states caused by tetravalent Cr capture photoexcited electrons.
(b) When the Fermi level is high, the water splitting reaction is accelerated because trivalent Cr becomes dominant and electron capture is inhibited.

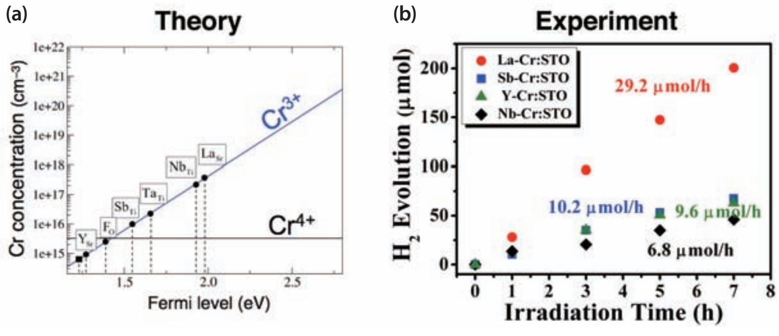


Fig. 2 Theoretical prediction of hydrogen generation efficiency and verification experiment
(a) Relationship between the position of the Fermi level and the Cr^{3+} concentration for the cases of doping the respective elements. The concentration of Cr^{3+}, which accelerates photocatalytic activity, was theoretically predicted to become the highest when Sr was replaced with La.
(b) Experiment of hydrogen generation through water splitting under visible light irradiation, using samples for which Cr and the respective elements (La, Sb, Y or Nb) were co-doped into $SrTiO_3$. It was experimentally confirmed that the activity becomes the highest when La and Cr are co-doped, thus demonstrating the validity of the theory.

Press release title: **Success in Theory-Driven Development of Photocatalyst**
—Expected to Accelerate Technologies for Producing Hydrogen from Water using Solar Light—
Press release date: January 22, 2013
URL: http://www.nims.go.jp/news/press/2013/01/p201301220.html

INTERVIEW

Interview with Dr. Naoto Umezawa

Dr. Umezawa addresses challenges through a theoretical calculation approach toward his big dream of realizing artificial photosynthesis. Behind this is his strong determination not to leave a negative legacy to the next generation.

——You have succeeded in the theoretical design of photocatalysts that exhibit high water-splitting activity under visible light irradiation.

Since I have engaged in development in the materials field while specializing in theory, I have always been thinking about making a contribution to society. This success results from the endeavor to somehow respond to the request of Dr. Ye, the project leader, and other researchers.

——What made you take an interest in theoretical calculation?

I had been interested in environmental energy issues since when I was young, but I focused my curiosity on theoretical study, and majored in computational science in school, studying first principles calculation. After I became a theory professional, I realized that the way is open to contribute to resolving problems such as environmental issues, and started my research on photocatalysts. I think these things fitted together well in my achieving the results in this research.

——The role of computational science seems to be ever growing.

The results in this research were one of the successful outcomes, but looking at photocatalysts alone, we must further investigate their various aspects and achieve high-accuracy design. There are a variety of tasks to be accomplished, such as closely examining the chemical reactions at the surface, and identifying the detailed paths through which electrons excited by absorbed light pass. This time, we implemented the materials design by only looking at one aspect, that is, within the scope of improving dopants. In order to determine which dopants should be selected, we theoretically predicted the conditions that improved the activity, by focusing only on the aspects of the Fermi level and the oxidation number of chromium. When we actually created the photocatalyst, it happened to work out. In any case, it is extremely difficult to predict an unknown photocatalyst.

——Will you continue specializing in photocatalyst research?

Photocatalysis phenomena are highly complicated and difficult to approach theoretically. It is very challenging, but rewarding. So I would like to continue with the research by all means. In particular, I want to give top priority to finding a breakthrough for realizing high-efficiency artificial photosynthesis, which is the ultimate challenge facing photocatalyst application. Also, if I get the chance, I hope to target solar cells and thermoelectric materials. No matter what, I want to contribute to resolving the energy issues facing us today.

——What theme did you study in school to earn your degree?

The development of electronic state calculation techniques. Specifically, developing new calculation techniques to analyze subjects that were difficult to handle by conventional methods. In the doctoral course, I was spending all my time doing calculations by hand and writing programs for numerical computation, which was far from materials research. Regrettably, however, it was difficult to find a job with such basic research, so I began materials research out of necessity. At first, I suffered great distress due to the dramatic change in my research theme. It took me two years to be able to study materials with interest. Now, I am glad that I went through such a struggle. It made me realize that there may be a more interesting world lying outside the research subject of my interest. Especially when you are young, it is important to engage in work outside your expertise, and to broaden your capacity as a researcher.

——Please tell us about your future research.

Of course, I want to further my research centering on materials. Conventional materials development had mainly been trial-and-error search through experiments. It was a very scattershot approach, and consumed enormous amounts of time. However, if we can give a guideline for narrowing the search domain by theoretical calculation, speedy development would become possible. Collaboration between experiment and theory is extremely important.

——What is your dream or goal?

I want to realize artificial photosynthesis that generates fuel from carbon dioxide and water by using sunlight with high efficiency. To that end, it is indispensable to integrate theory and experiment to find a breakthrough. So as not to leave a negative legacy to the next generation, my goal is to accomplish this in around 15 years' time when my son has grown up.

Profile

Naoto Umezawa Ph.D. Completed the doctoral course in the Department of Physics, University of Tokyo Graduate School of Science, and was employed as a Postdoctoral Scientist at the University of Southern California in 2003. Joined NIMS as a Special Researcher in 2004 and was appointed to his present position as Senior Researcher at NIMS in 2008. In 2007, he was a Visiting Scientist at the University of California at Santa Barbara. He also received the 29th Japan Society of Applied Physics Best Original Paper Award in 2007. His research field is materials design using first-principles calculation.

PRESS RELEASE

Development of High Sensitivity Detection Method for Trace Amounts of Mercury in Water

Group Leader, Nano-System Photonics Group, Nano-System Organization Unit,
Nano-System Field, International Center for Materials Nanoarchitectonics (MANA)
Tadaaki Nagao

Trace amounts of mercury in water are difficult to detect

Mercury is a serious environmental pollutant which is hard to control and decontaminate. In everyday products, it is also emitted from wastes of dry cell batteries, fluorescent tubes, thermometers and so on. Mercury is easily vaporized at room temperature and diffuses in the atmosphere.

In water, mercury dissolves in the form of atoms (Hg^0) and ions (Hg^{2+}), and some of such mercury in the form of an organic mercury compound caused Minamata disease.

Conventional methods for detecting trace amounts of mercury contamination, such as gas chromatography, can detect mercury at the level of parts per billion (ppb) or parts per trillion (ppt), but they require expensive dedicated equipment. There are a lot of study also on the colorimetric assay method where mercury is detected based on the color of a reagent that reacts with mercury, but its sensitivity is only at the level of parts per million (ppm), presenting a problem in terms of accuracy.

New material was developed in order to use a simple infrared absorption spectrometer

As a cost-effective, simple and higher-sensitivity detection method, we considered use of an infrared absorption spectrometer. Infrared spectroscopy can measure atomic and molecular vibrations of a material with high sensitivity, but it was difficult to use when measuring in water because the strong vibrational spectrum of the water itself hides the spectrum of the target analytes.

Thus, we newly developed a material which is a gold nanostructure with nanoscale gaps (nanogaps) coated with linker molecule (DNA) aptamer which can selectively absorb ionic mercury (Fig. 1 (a)(c)). By strongly concentrating the electromagnetic field in these nanogaps, the background spectrum of water can be dramatically reduced, and further, the spectrum of molecular vibration can be enhanced.

Experiment using the actual natural water of Lake Kasumigaura

In this experiment, we used the natural water of Lake Kasumigaura (Fig. 1 (b)). After simply filtering the sludge in the collected water, we added a trace amount of mercury (II) chloride solution ranging from 36.8 ppb to 36.8 ppt, and conducted infrared absorption spectroscopy under attenuated total reflection conditions.

When the DNA aptamer absorbs ionic mercury in a gold nanogap, the structure of the DNA aptamer changes, and a peak occurs in the enhanced infrared spectra. As a matter of course, the obtained spectrum includes the spectra of amino acids and proteins from living organisms in Lake Kasumigaura, but since they are well separated from the spectrum of mercury, they hardly affect the measurement of mercury.

Measurement of ions without molecular vibration made possible

While infrared absorption spectroscopy measures molecular vibration, in this research, we succeeded in detecting metal ions in water which do not have molecular vibration, by using natural water without special pretreatment and a standard, low-cost Fourier transform infrared (FT-IR) spectrometer.

Compared to other methods for analyzing water using light,* our method shows better results by one to two orders of magnitude.

This research suggests that the widely used infrared spectroscopy has sufficient potential for being applied to measurement of trace amounts of metal ions dissolved in water. Furthermore, we confirmed that some of the peptides in human body also act as efficient aptamer linker molecules for trapping mercuric ions, which may be more efficient in cost and sensitivity for the detection of pollutants in water. We have tested the performance of such peptides using SiO_2 nanospheres loaded with Au nanogap islands (Fig.2).

This research has provided important results that broaden the possibilities of sensing using infrared light, and is expected to be useful in water quality management and monitoring of biomaterials.

* Such methods include surface plasmon sensing and surface enhanced Raman scattering.

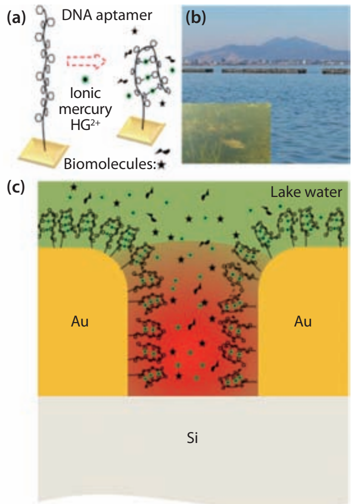


Fig. 2 **(a)**Schematic of the surface coating material (DNA aptamer). Only the ionic mercury is selectively absorbed; biomolecules are not trapped. **(b)**Lake Kasumigaura, where the natural water was sampled. **(c)**Schematic of a nanogap on the gold surface, which was coated with the surface coating material. (Collaboration with C.V. Haong, M. Oyama, M. Aono)

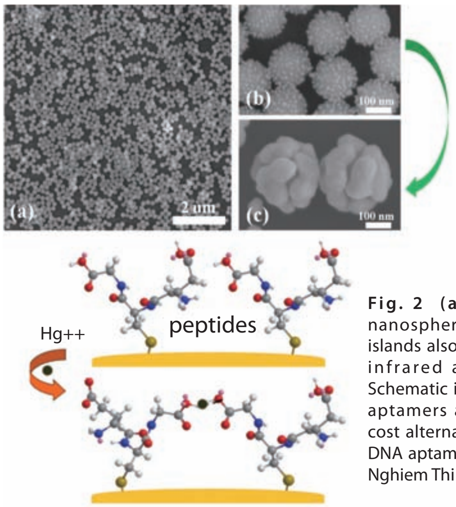


Fig. 2 **(a)-(c)** Fabrication of SiO_2 nanospheres loaded with Au nanogap islands also useful for the high-sensitivity infrared absorption spectroscopy. Schematic illustration of the peptide Hg^{2+} aptamers as high-sensitivity and low-cost alternative for the above mentioned DNA aptamer in Fig. 1. (Collaboration with Nghiem Thi Ha Lien and Thang Duy Dao)

Press release title: **Development of High Sensitivity Detection Method for Diluted Ionic Mercury in Water**
Enabling High Accuracy Monitoring and Early Discovery of Mercury Contamination in Lacustrine Environments
Press release date: February 6, 2013
URL: http://www.nims.go.jp/eng/news/press/2013/02/p201302060.html

INTERVIEW

Interview with **Dr. Tadaaki Nagao**

Dr. Nagao says the idea underlying this research result is to see what people cannot see. Also, his strong devotion to develop not a mere idea but a material that can be used in a real environment seems to have led to this successful result.

—You developed a method to detect trace amounts of mercury using the water of Lake Kasumigaura.

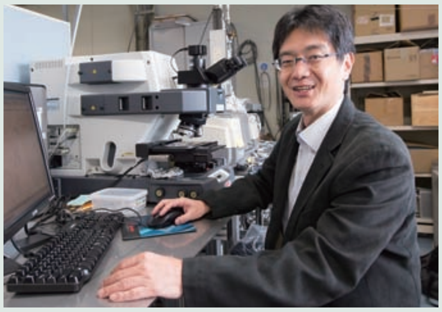
It is not that the water of Lake Kasumigaura contains mercury. It was important to use real lacustrine water that contains bacteria and other various natural things. We added an unbelievably small amount of mercury to the water, and tested whether we can detect it. I used the water of Lake Kasumigaura because I often went to the lake for fishing with my family, and I had a strong desire to use real water from a natural environment. Even if we could verify the idea in the laboratory, it would be of no use if the method could not be used in reality.

—Was there any reason for choosing mercury as the target to be detected?

The mercury contamination issue has been in my mind since about two years ago through the discussions with our group member. Not as a domestic issue but a global issue. For example, discharge of mercury from coal power plants in India and China has been considered as a problem recently. Japan is also increasing coal-fired power generation in place of nuclear power generation. After we achieved this research result, we received comments from overseas encouraging us to continue with the development because, while research for detecting mercury in the atmosphere has made progress, that for detecting mercury in water is quite rare.

—What was your research theme in school?

When I was in school, I specialized in thin films and ultrahigh vacuum physics. My PhD thesis advisor at the time (Professor Chuhei Oshima at Waseda University) placed the utmost importance on seeing what people cannot see. The shortest way to that goal is to make equipment by yourself. I was engaged in making prototypes of electron energy-loss spectrometers and measuring phonons on a solid surface, and my activity centered on the development of equipment. It was "in a vacuum" then, and now "in water." Of course, water and vacuums are completely different, but the theme has not changed up to the present in that I am studying low-energy phenomena involving light with micrometer-scale wavelengths and excitations with sub-electron volts to millielectron volts.



—You were seeing or measuring things based on molecular vibration and wavelengths.

That's right. After I graduated from graduate school, I took a job as a research associate at an electronic property laboratory in the University of Tokyo, and helped with research on electronic states and electric conduction. I had a chance to study both atom waves and vibration at school and electron waves at work. This lucky change in the field made me capable of coming up with new ideas. This is the core part of my background.

—You joined NIMS in 2004.

At first, I joined NIMS as a director candidate for bio research under Dr. Aono's center. For example, I formed an optical resonator structure with atomic wires on a semiconductor, and measured plasmons, which are electron waves, by infrared spectroscopy. I also placed emphasis on bio measurement techniques. After growing gold on a silicon surface, I created nano-level gaps while monitoring with light, and made it possible to control the gap size. I am trying to measure bio-related materials, such as proteins, based on the electric field enhancement effect that occurs at those gaps.

—So, did you achieve this research result by combining such infrared resonator structure and the control of gold nanostructures?

Yes. There was an atomic-level resonator at first, and then I tried with a slightly larger resonator to match the size of DNA. It was an arbitrary system, not a clearly-designed system like a resonator or an antenna, but when I tuned the gap size and film thickness of this arbitrary system, it exhibited good properties. Not many researchers have studied structural control of such a system in water. When we measure a material using infrared light, the water absorption will be large, and we won't be able to see the material, but when we bring the electric field between the gaps of gold to a pin point, we can selectively see what is in the gaps. When I actually tried this, I could confirm selective signaling, and it worked well.

—The detection limit of this method is said to be one to two orders of magnitude better than that of other detection methods. Why is this?

That is because mercury can be detected at the ion level. In fact, it is unconventional to measure ions with vibration spectroscopy. Since an ion consists of a single atom, it does not cause vibration like molecular vibration, and cannot be measured. However, when it is trapped by a molecule (aptamer), the vibration frequency of the molecule changes, so we measure that change in frequency. We have to make new twists to old ideas. In the case of a protein, we can see the protein itself based on the enhancement effect of gold, but that is not enough when trying to see metal ions.

—What is your future dream?

As I touched upon earlier, I also have a dream in the bio-related field. For example, measuring pathogenic enzymes in blood, or using a polymer as a sensor by embedding metal nanostructures. There are so many things mixed together in blood that it is extremely difficult to selectively measure a specific material included therein. The key to success would be the choice of the linker molecule. In the future, I want to develop a method to detect or measure materials only by using a physical method, without depending on linker molecules.

Profile

Tadaaki Nagao D. Sci. Left Graduate School of Waseda University in 1994. After working as Research Assistant at the Kagami Memorial Research Institute for Materials Science and Technology at Waseda University, Research Associate at Faculty of Science, University of Tokyo, Associate Professor at Institute for Materials Research, Tohoku University, joined NIMS in 2004.

PRESS RELEASE

Layered Crystal Expands and Shrinks Like Accordion in Aqueous Solution

MANA Principal Investigator,
International Center for Materials Nanoarchitectonics (MANA)
Takayoshi Sasaki

MANA
Renzhi Ma

MANA
Fengxia Geng

Interlayer space widens substantially, causing delamination

An inorganic layered crystal has a mille-feuille structure with stacks of layers formed by atoms strongly bonded in the horizontal direction. It exhibits reactivity called "intercalation," which inserts molecules or ions between the layers. Since the intercalation can cause a dramatic change in the physical properties or form a sort of nanocomposites with an organic moieties, considerable research has been conducted on inorganic layered crystals.

In some cases, when the crystal is reacted with an aqueous solution containing specific amine compounds, the crystal intercalates a large amount of water along with amine between its layers. Because the interlayer space substantially widens and the force acting between the layers weakens as a result, the crystal delaminates into separate layers in many cases, generating extremely thin 2-dimensional crystals corresponding to the number of atoms.

These 2-dimensional materials called nanosheets are drawing much attention since they exhibit new functions and reactivities that are not observed in conventional materials. A representative example is graphene consisting of a single layer of graphite, for which the Nobel Prize in Physics was awarded in 2010. In this manner, the swelling phenomenon of layered crystals is a vitally important reaction for the synthesis of such 2-dimensional materials.

Expectations for furthering the understanding of the largely unknown behavior of water

Recently, we have discovered an interesting phenomenon whereby a plate-shaped lamellar crystal expands like an accordion to 100 times its original length in 1–2 seconds, in an aqueous solution containing traces of compounds called amino alcohols.

We found that the crystal expanded in a string-like manner remains stable without breaking, and returns to its original state in several seconds by adding an acid.

Whereas the lamellar crystal used in the experiment is comprised of a stack of around 3,000 layers each with a thickness of almost 1 nanometer and consisting of titanium and oxygen atoms, a huge volume of water, sufficient to uniformly swell the interlayer spaces as much as 100 times, goes in and out of those spaces in an extremely short time, and in this process, the crystal behaves as a monolith without separation of the layers. While why such incredible swelling state remains stable is interesting, unlike in the case of ordinary amine which promotes delamination, theoretical calculations showed that the water between the layers has a special state, with a strong, tough hydrogen bond network of water molecules being developed with the amino alcohols used for the reaction serving as the point of origin.

The data obtained in this research is expected to enhance the understanding of the swelling and delamination phenomena of layered materials, which are still largely unknown, and lead to the synthesis of high-grade 2-dimensional materials such as graphene and nanosheets.

In addition, this discovery has the potential of shedding light on the unique behavior of water when enclosed in confined spaces, which is a key factor in biological phenomena and catalytic reactions, but is still an area where many questions remain unanswered.

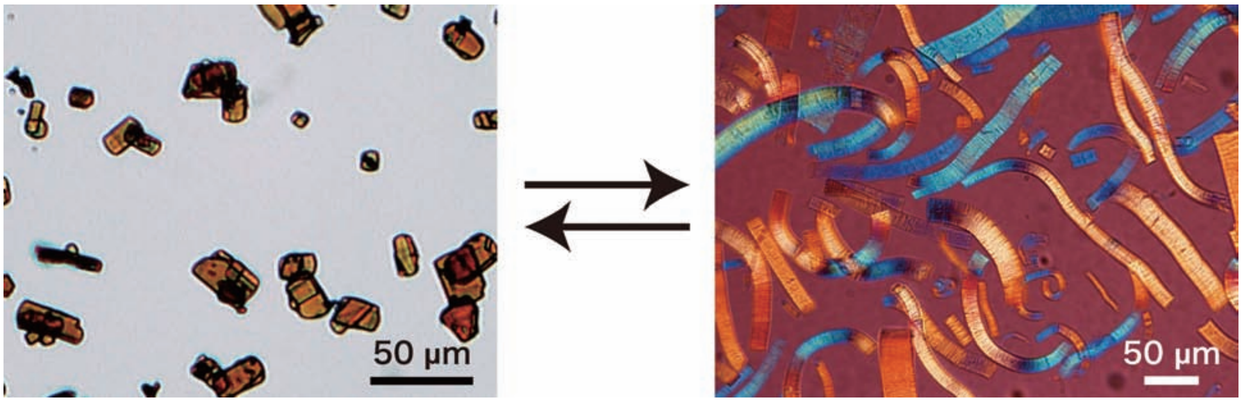


Fig. 1 Plate-shaped lamellar titanium oxide crystal (left) and the state of substantial swelling in an aqueous solution of amino alcohol (right; a polarizing microscope image)

Press release title: **Discovery of New Gigantic Swelling Phenomenon of Layered Crystal Driven by Water**
Potential to Open the Road to Elucidation of the Behavior of Water in Nanosheet Manufacturing Technology and Biological Phenomena

Press release date: March 25, 2013
URL: http://www.nims.go.jp/eng/news/press/2013/03/p201303280.html

INTERVIEW

Interview with Dr. Takayoshi Sasaki

Even Dr. Sasaki, with experience studying layered materials for 30 years, was astonished to discover that layered crystals can swell 100 times in water. He says accumulating such discoveries is one of the joys of research and leads to further development.

— The fact that a thin plate-shaped material swells as much as 100 times in water is a stunning discovery.

Although it is a research result in the field of basic science, it received tremendous reactions from people who were surprised at how much the material swells.

— So, water has interesting properties.

Indeed. I have learned since my school days that water plays critical roles in various reactions. However, such roles have not been fully understood quantitatively. In that sense, I think water is an eternal research theme. We happened to come across this property of water in the process of delaminating layered materials into single layers.

— What made you start engaging in research on layered compounds?

When I joined the National Institute for Research in Inorganic Materials, the predecessor of NIMS, 30 years ago, the group leader specified layered materials as my research theme. The group I was assigned to had been studying titanium oxides at the time, doing research on the tunnel structure on one hand, and on layered materials on the other. Being told to study layered materials, I was investigating how structures and properties changed by making various materials go in and out of the interlayer spaces of layered titanium oxide. It was very low-profile research, but I reacted layered materials with various other materials and found that the material turns into something like milk under certain conditions, and the layered material swells huge and finally turns into nanosheets. It was surprising that the layered material swells to finally delaminate, going into such a state.

— Was there anything you found particularly impressive as a researcher?

Of course, I was impressed to find that a layered material swells enormously large and delaminates as its ultimate form. However, I was also excited when I tried to delaminate a layered cobalt compound, and although it did not delaminate, I found that it turns into a superconductor under certain conditions. Such accumulation leads to research and development of nanosheets, and brings me joy as a researcher on various instances, although each finding may be small.

— Will these layered materials provide useful materials in the future?

One interesting idea is to stabilize this swollen crystal by turning it into hydrogel. A layered material only swells within a solution (water). When it is taken out of the water, it dries up. Thus, if we add in advance a small amount of materials (monomers) for forming polymers to the solution, and if we cause polymerization after the swelling, and form a polymer network, we may be able to extract the swelling state in a stable manner. If that is possible, it could give rise to unexpected applications. Also, because it is a phenomenon within water, we found that the stability of the swelling can be changed by changing the reagent for the swelling. Thus, by controlling the delaminating process, we may be able to create high-quality 2-dimensional materials. I always want to dream big.

— I look forward to your further research. Thank you very much.

There are still many more things to look into. I would like to continue with not only trendy but also down-to-earth research with a focus on layered materials.

Profile

Takayoshi Sasaki D. Sc. Received his PhD in Chemistry from the University of Tokyo in 1985. Joined NIRIM (reorganized into NIMS in 2001) in 1980. NIMS Fellow and MANA PI.

PRESS RELEASE

Development of Nanofiber Mesh Capable of Simultaneously Performing Thermotherapy and Chemotherapy

MANA Scientist, Smart Biomaterials Group,
Biomaterials Unit, Nano-Life Field,
International Center for Materials Nanoarchitectonics (MANA)
Mitsuhiro Ebara

Development of a material capable of simultaneously performing thermotherapy and chemotherapy

Squamous cell carcinoma (SCC)[1] is an epithelial malignant tumor found in mucous membranes lined by stratified squamous epithelium and in the skin. At present, the main therapeutic methods for SCC are surgery, radiation therapy and chemotherapy, according to the stages of the cancer.

In recent years, thermotherapy (hyperthermia[2]), which takes advantage of the fact that cancer cells are more sensitive to heat than normal cells, has attracted great attention. Since thermotherapy is also effective for enhancing drug efficacy and relieving pain, high expectations are placed on its combined use with chemotherapy and other types of therapy.

In this research, we developed a mesh material which can be applied directly to the affected part, and which is capable of simultaneously performing thermotherapy and chemotherapy for treating epithelial malignant tumors (Fig. 1).

Effects measured by placing the nanofiber mesh on cancer cells

We processed a temperature-responsive polymer into nanofibers by electrospinning,[3] and created a nonwoven fabric (Fig. 2). In this process, we included magnetic nanoparticles in the fibers. As a result, we succeeded in heating the fibers by causing self-heating of the magnetic nanoparticles contained in the fibers through application of an alternating magnetic field.

Furthermore, the temperature-responsive polymer dehydrates in response to the heat generated by the magnetic nanoparticles, enabling external release of anticancer drugs contained in the nanofiber mesh together with water in the mesh.

When we investigated the anticancer activity of this fiber by using a human melanoma cell strain, we found that it is possible to drastically inhibit cancer cell growth by applying an alternating magnetic field.

Compared to cases of separately administering fibers containing magnetic particles and fibers containing anticancer drugs, the highest killing power (70%) was observed when nanofibers containing both of these were added to the cells (Fig. 3a).

In addition, as a result of performing Annexin V and TUNEL staining in order to assay early apoptosis and late apoptosis, we detected fluorescence when we added a nanofiber mesh containing anticancer drugs and magnetic particles (Fig. 3b). This result suggests apoptosis of the cancer cells. In other words, we succeeded in effectively inducing apoptosis[4] of cancer cells by placing a nanofiber mesh on those cells and applying an alternating magnetic field.

Arbitrarily causing disappearance of cancer cells in an effective manner

Due to the progress in therapeutic techniques, recently, it has become possible to treat cancer cells that remain within a mucous membrane by such methods as endoscopic therapy. Thus, development of a mesh material which is easy to handle and which exhibits anticancer activity itself is considered to lead not only to improving the survival rate of cancer patients but also to providing minimally invasive treatment methods.

A possible treatment method using this material would be to directly affix the mesh to the affected part after endoscopically removing the cancer, and apply a magnetic field from outside at an arbitrary timing, in order to cause the disappearance of cancer in an effective manner. Since this material can also easily contain various materials other than anticancer drugs and magnetic particles, it has the potential to be used in combination with near infrared responsive materials which easily penetrate through living tissues or with other drugs, and furthermore, lead to the development of more functional fiber mesh by adding biodegradability or other functions.

1) Squamous cell carcinoma: An epithelial malignant tumor found in a mucous membrane lined by stratified squamous epithelium, such as the oral cavity, tongue, pharynx, esophagus, vocal cord, trachea, larynx, anus, vulva, vagina, uterine cervix, and vaginal portion of the cervix, and in the skin.
2) Hyperthermia: It usually means thermotherapy for cancer using a temperature of around 40–45°C, but it is also used for purposes other than cancer treatment, such as enhancing drug efficacy and relieving pain.
3) Electrospinning: A technique to spin fibers by spraying ultrafine jets of a polymer solution from nozzles toward an electrode on which the sprayed solution is collected.
4) Apoptosis: A form of death of cells constituting multicellular organisms. In contrast to necrosis, which is cell death caused by deterioration of the environment in or outside the cell, apoptosis is cell suicide, or programmed cell death, which is actively triggered in order to keep the individual organism in good condition.

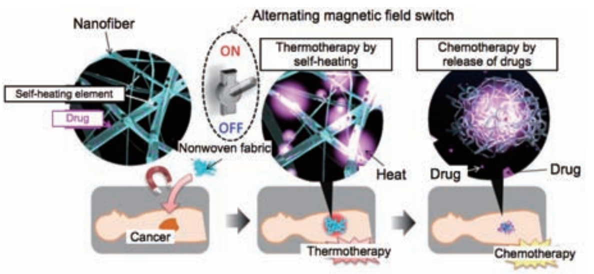


Fig. 1 Cancer treatment using a nanofiber mesh with self-heating and anticancer drug releasing functions.

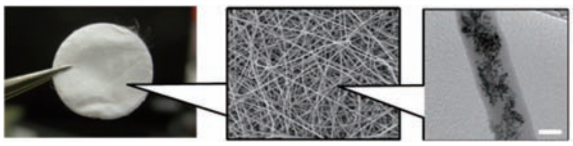


Fig. 2 SEM (middle) and TEM (right; bar 200 nm) images of a nanofiber mesh.

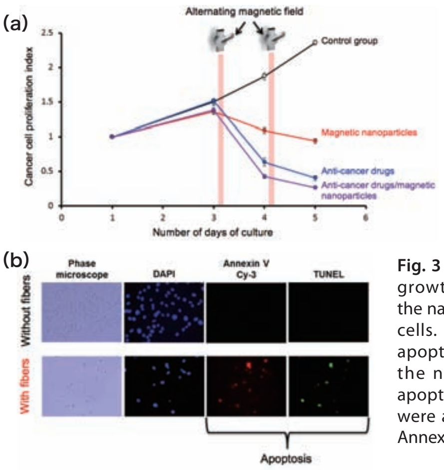


Fig. 3 **(a)** Experiment on the growth inhibitory effect of the nanofiber mesh on cancer cells. **(b)** Experiment on the apoptosis inducing effect of the nanofiber mesh. Early apoptosis and late apoptosis were assayed by performing Annexin V and TUNEL staining.

Press release title: **Smart Anticancer "Nanofiber Mesh"**
Success in Inducing Natural Death of Epithelial Cancer Cells by Simultaneously Realizing Thermotherapy and Chemotherapy

Press release date: June 14, 2013
URL: http://www.nims.go.jp/news/press/2013/06/p201306140.html

INTERVIEW

Interview with Dr. Mitsuhiro Ebara

How can polymer research contribute to the medical field? Dr. Ebara who continues to pursue this major theme tells us about the background of this research result and his future dream.

––Is the material used for the fiber you developed in this research different from conventional polymers?

I used a material called a smart polymer, which changes its own properties in response to the surrounding environment. For example, it can be responsive to temperature, pH, magnetic fields or electric fields. Simply put, such a polymer is processed as a raw material into fibers and particles.

––Is it common to process a smart polymer into nanofibers?

No, it is quite rare. I think that is the unique part of this research. The created fiber mesh is large enough to be held by hand, and each fiber is about 500 nm in diameter. The fiber is a collection of hundreds of polymers. Each polymer is only several nanometers in diameter, but the polymers are collected together to form a single fiber. When creating the fiber, nano particles that are responsive to magnetic fields and anticancer drugs are included in the fiber. In that process, there will be a great difference depending on whether the polymers are branched or not, and whether the bonded parts of the polymers are 5 nm or 2 nm.

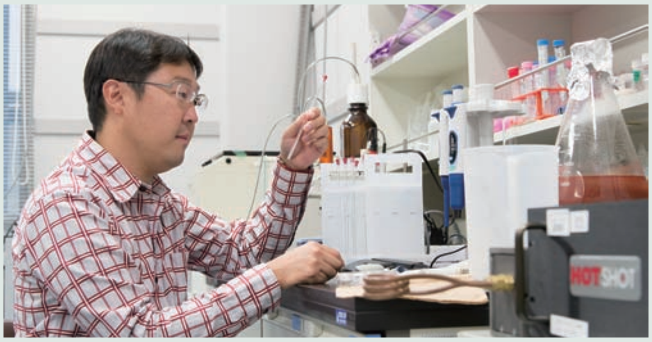
––The developed research encompasses diverse elements, ranging from polymers and magnetic fields to drugs.

In that sense, I think being at NIMS made this research possible. When we try to materialize an idea in research at, for example, a medical university, we usually look for and bring materials from outside. However, since NIMS specializes in materials research, we can create the materials from scratch. Instead of using something that already exists, we can make everything by ourselves. Also, while our expertise is polymer materials, and magnetic particles are outside our domain, NIMS has a strong edge in metals and ceramics, so we were able to clear that hurdle. In addition, the MANA environment contributed significantly to our research as well. Since there are world's top-level researchers at MANA, we were able to receive various advice from them.

––What was the most difficult part?

Technically, the hard part was designing the size of the nano-scale lattice so that magnetic particles cannot come out of the fiber but anticancer drugs can. Because the size of the magnetic particles is fixed, we made the polymer have a mesh structure that can effectively confine the particles. I guess that is what we call nanoarchitectonics.

When the goal is writing an article, it does not matter so much whether the final drug release temperature is 43°C or 42°C. Since my previous job was conducting clinical research on humans at Osaka University, I did not want to set an article as my research goal from such experience. I wanted to achieve results that are accurate enough to be used in a clinical setting. That was the most difficult part. The fiber diameter, the drug release temperature and amount—we designed all these precisely in consideration of clinical application. After the press release, we directly received responses from patients. Their reactions made me strongly feel that this is the start.



––Was this research prompted by surgeons?

Originally, idea of applying smart polymers to medical care was one of my research theme from college days. In this research, a surgeon, who is a partner in joint research with me, proposed an idea of making something like an adhesive plaster with a drug soaked into it. We at NIMS, particularly MANA, focused on nano materials, and considered using nanofibers instead of mere films so as to be able to release drugs, and enable surgeons to control the timing of the release, and, further, perform thermotherapy. Since smart polymers excel the most at achieving such combination of functions, that part of the research went extremely smoothly.

––What is your future dream?

We focus on medical care in low-infrastructure areas. For example, we are also studying diagnosis systems that can be used for testing diseases such as malaria, without electricity or water and under the blazing sun, in Africa and other developing countries. Under such conditions, cost is also a major problem. In that respect, smart polymers can generate heat by finger friction, and can also use solar light. We want to aim at what we call "material therapy," which uses materials that can be driven without electricity or water—extremely speaking, treating cancer or curing myocardial infarction by only using polymers, for instance. One possible idea is to use a shape-memory polymer to control cell growth by applying force from outside. It is a huge theme that could take about fifty years (laughter), but that would be my dream.

Profile

Mitsuhiro Ebara Ph. D. (Eng.) Completed the doctoral course at the Waseda University Graduate School of Science and Engineering in 2004. Prior to joining NIMS, he was a doctoral researcher in the Department of Bioengineering at the University of Washington in the United States and doctoral researcher at the Bill and Melinda Gates Foundation. Appointed to Special Assisstant Professor of the Osaka University Hospital in 2007. Present position as a MANA Scientist since 2009.

NIMS NEWS

1 NIMS Researchers Win Tsukuba Encouragement Prizes

On November 26, Dr. Shiro Torizuka (Station Director, Materials Manufacturing and Engineering Station) and Dr. Genki Yoshikawa (MANA Independent Scientist) received Tsukuba Encouragement Prizes.

The Tsukuba Encouragement Prize is presented annually to people whose research results have yielded practical applications or who otherwise made notable achievements or young researchers who are expected to make remarkable research achievements in the future, among those engaged in research in science and technology within Ibaraki Prefecture. The prize is in its 23rd year this year.

Dr. Torizuka, Station Director, won the Prize (practical application research category) for his research titled "Mass production of high-strength precision screws using nanostructuring of steel realized for the first time in the world: success in cutting CO_2 emissions by 50%." The high-strength screws developed in this research are expected to be used in a variety of fields including intelligent home appliances and medical care where high-strength precision components are needed.

Dr. Yoshikawa, MANA Independent Scientist, received the Prize (young researcher category) for "Development of a highly sensitive nanomechanical membrane-type surface stress sensor (MSS)." While the sensitivity of nanomechanical sensors had been enhanced only by several tens of percents over the past twenty years, he succeeded in raising the sensitivity by more than 100 times through the development of the MSS.

An awarding ceremony for these prizes was held together with that for the 10th Leo Esaki Award at the Tsukuba International Congress Center in Tsukuba City, Ibaraki Prefecture, and the prize winners gave commemorative speeches.

Dr. Torizuka (right) shaking hands with Dr. Reona Esaki (left) at the awarding ceremony.

Commemorative photo taken after the awarding.
Dr. Yoshikawa (center) with Dr. Esaki (left) and Mr. Ichihara, the mayor of Tsukuba City.

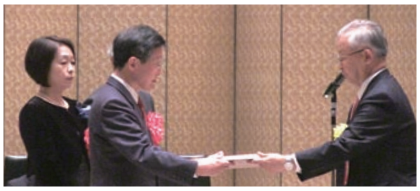
2 Yamazaki-Teiichi Prize Awarded for Development of Heat-Resistant Superalloy

On November 22, Dr. Hiroshi Harada (Senior Scientist with Special Missions), Dr. Kyoko Kawagishi (Senior Researcher) and Dr. Tadaharu Yokokawa (former Principal Researcher) of the Environment and Energy Materials Division were awarded the Yamazaki-Teiichi Prize from the Foundation for Promotion of Material Science and Technology of Japan.

The Yamazaki-Teiichi Prize is presented annually to people who have made outstanding, creative achievements that lead to the practical application of new materials, and marks its 13th year this year.

Dr. Harada, Senior Scientist with Special Missions, and his collaborators developed a nickel-based superalloy that boasts the world's highest level of heat resistance, and realized practical application of the superalloy in latest-model jet engines and gas turbines as a high-temperature turbine material. This turbine can combust fuel at a higher temperature than in the past, so it is able to cut CO_2 emissions.

The awarding ceremony was held at the Japan Academy in Ueno, Tokyo. After Dr. Hideki Shirakawa, chairman of the selection committee, explained the reasons for awarding the prize, an award certificate, a gold medal and prize money were handed to all winners. On behalf of the winners, Dr. Harada gave a presentation of their research.



Dr. Hiroshi Harada, Senior Scientist with Special Missions, receiving an award certificate at the awarding ceremony.

The three researchers receiving a commendation ([from the center to the right] Dr. Hiroshi Harada, Dr. Kyoko Kawagishi and Dr. Tadaharu Yokokawa; [at the very left] Dr. Hideki Shirakawa, chairman of the selection committee).

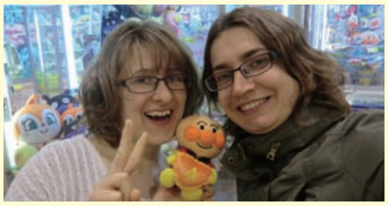
Hello from NIMS

Dear NIMS NOW readers,

A few months ago, I lost my wallet. Unbelievable - I got it back, including all its contents, via postal mail. I am not sure whether the postal charges were taken out or not. Probably not. This can only happen in one country - Japan. I have been living here for nearly five years, one of which I spent working in a German company and the rest at NIMS. Even after all those years the Japanese culture still manages to surprise me. It is not always easy, since the life style is quite different from my own, but it is certainly a great experience and I love it. Working in NIMS and living in Tsukuba gives me the opportunity to experience both Japanese and international culture, city and country life and the chance to do high-level research. I especially enjoy the diversity of the Japanese culture and the Japanese nature. Being in Japan certainly became a significant part of my life and who knows how long my stay will continue?

Riverside in Minakami before going rafting with friends.

Karolin Jiptner (Germany)
April 2010 – present
Postdoc, Department: Nano-Device Characterization Group, WPI MANA



We won, we won!

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cover image: Electrospinning apparatus

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