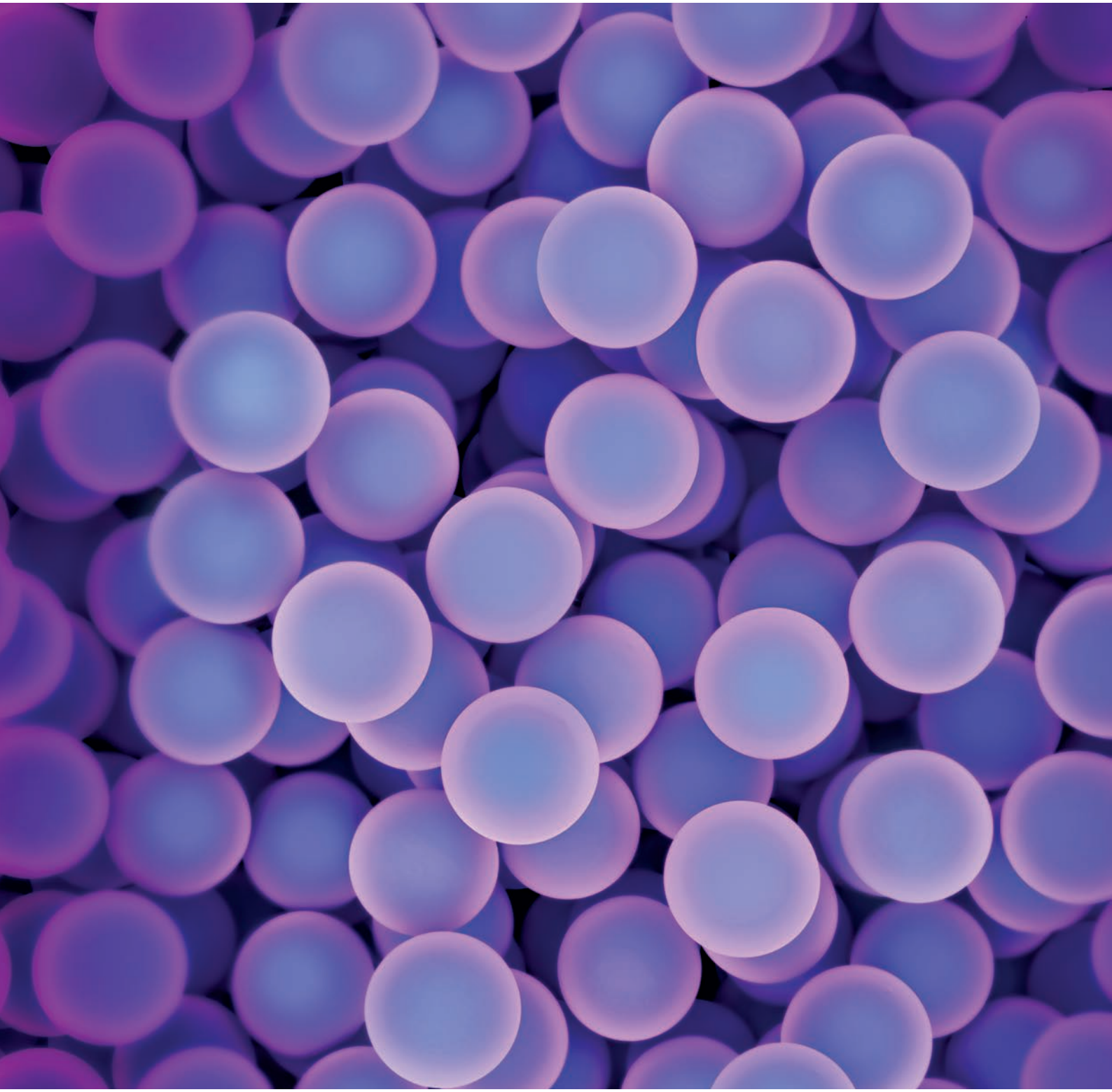
AiM Research

RESEARCH HIGHLIGHTS 2014

A publication of the WPI Advanced Institute for Materials Research



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WPI Advanced Institute for Materials Research

The Advanced Institute for Materials Research (AIMR) at Tohoku University in Sendai, Japan, is one of nine World Premier International Research Center Initiative (WPI) programs established with the support of the Japanese Ministry of Education, Culture, Sports, Science and Technology (MEXT). Since its inauguration in 2007, the AIMR has been bringing together world-class researchers from Japan and abroad to carry out cutting-edge research in materials science through interdisciplinary collaboration among its four groups — Bulk Metallic Glasses, Materials Physics, Soft Materials, Device/System — and Mathematics Unit, with further integration supported by its Interface Unit.

Led by distinguished mathematician and director Motoko Kotani, the institute promotes interdisciplinary research across the different groups while fostering young researchers through the Global Intellectual Incubation and Integration Laboratory (GI^3 Lab), where international joint research is carried out in close cooperation with high-profile researchers invited from countries throughout the world.

The AIMR is host to over 150 leading researchers, around half of whom come from abroad, including 30 principal investigators. In addition to the research hub at Tohoku University, the AIMR collaborates with research centers in China, France, Germany, Poland, the United Kingdom and the United States. Close ties with other leading overseas institutes are maintained through its Adjunct Professor and Associate Professor programs.

AIM*Research*

AIM*Research* is an online and print publication that highlights the scientific achievements and activities of the AIMR. First published in June 2009, AIM*Research* selects the most important papers from the wealth of research produced by AIMR scientists throughout the year, distilling the essence of the achievements into timely, concise and accessible research highlights that are easy to digest, but retain all of the impact and importance of the original research article. Published monthly on the AIM*Research* website in both English and Japanese, AIM*Research* research highlights bring the very best of AIMR research to a global audience of specialists and nonspecialists alike. AIM*Research* also publishes a range of feature articles introducing other activities of the AIMR's research groups. Visitors to the website can register for monthly email alerts in either English or Japanese to keep abreast of the latest developments and discoveries made at the AIMR.

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Editorial
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MESSAGE FROM THE DIRECTOR

Creating a global community of research collaborators in mathematics and materials science

As the director of the Advanced Institute for Materials Research (AIMR), Tohoku University, it is my great pleasure to share with you the sixth print edition of AIM*Research: Research Highlights*. AIM*Research* highlights the best of the AIMR's research through a bilingual English–Japanese website. This print collection compiles all the research highlights and feature articles published online in 2014. It provides an overview of our scientific achievements and introduces our researchers and activities.

The AIMR was established in 2007 under the World Premier International Research Center Initiative (WPI) program initiated by the Japanese Ministry of Education, Culture, Sports, Science and Technology (MEXT) to support the development of world-class research centers in Japan. Since its foundation, the AIMR has been actively conducting research and creating new material systems. We strive to maintain our standing as a global center for materials science with an attractive research environment for the world's best minds.

The AIMR pursues collaboration between mathematics and materials science to accelerate interdisciplinary fusion and to explore new materials science by generating theoretical predictions. Such institution-level collaboration is unprecedented and has invited significant interest from both the materials science and mathematics communities. Mathematicians and experimentalists at the AIMR conduct joint research, discuss problems and develop new models together, which has led to remarkable progress, as evidenced by the many published papers with a mathematical viewpoint in high-impact journals.

In 2012, to clarify the goals of our mathematics–materials science collaboration, the AIMR set up three Target Projects: Non-equilibrium Materials based on Mathematical Dynamical Systems; Topological Functional Materials; and Multi-scale Hierarchical Materials based on Discrete Geometric Analysis. This year, we started working in earnest on a fourth project, Core Technology for Nano Energy Devices. By applying the results of the three fundamental projects, this fourth project aims to produce new devices and systems that will directly benefit society.

Ultimately, the AIMR's goals are to deduce scientific principles for controlling atoms and molecules based on theoretical predictions and to create new functional materials, devices and systems that will enhance the safety and quality of life for communities.

The AIMR has implemented several organizational reforms, which have contributed to it

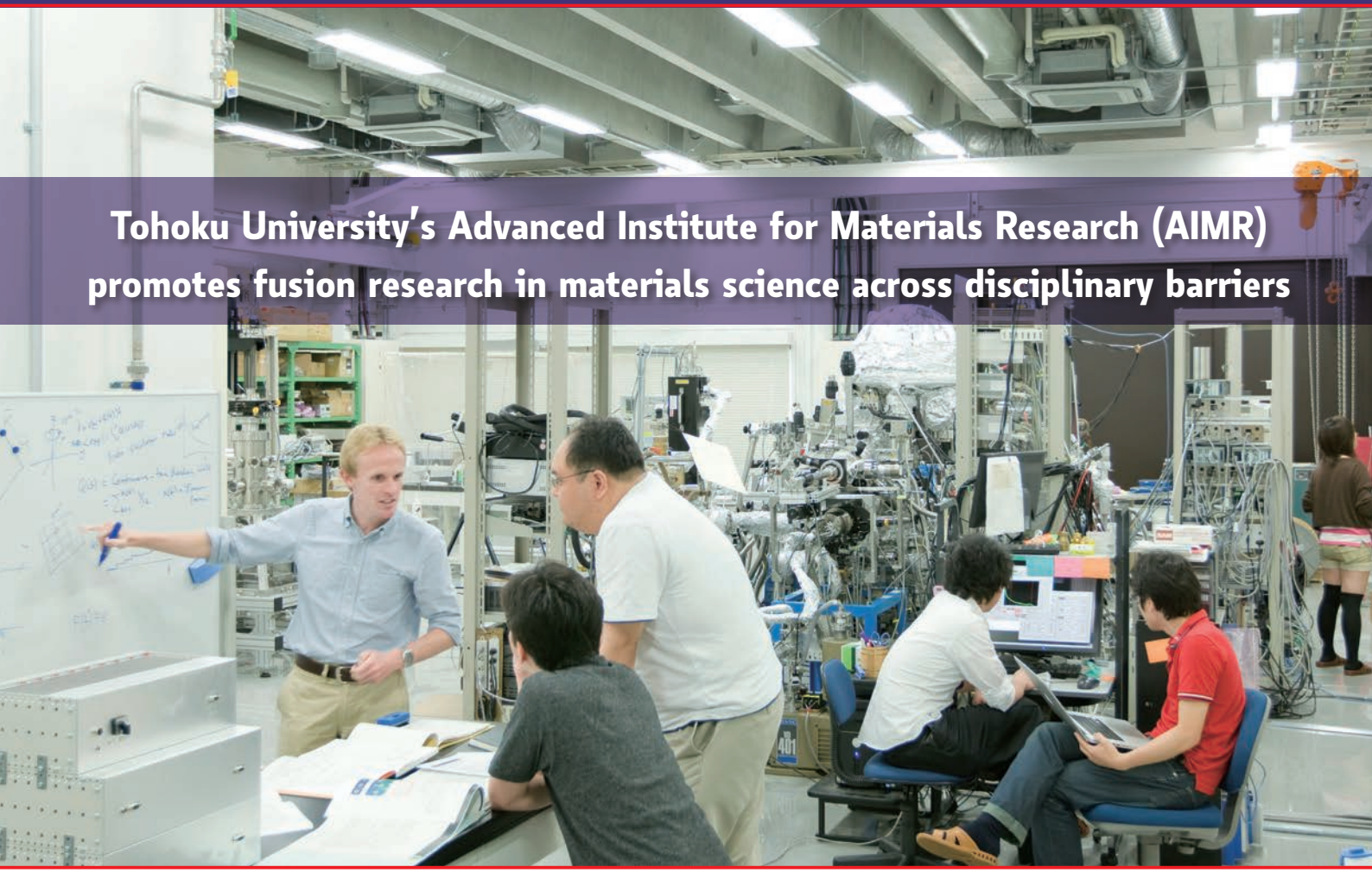
becoming a world-leading institute for materials research. This year, Tohoku University set up the Organization for Advanced Studies (OAS) to promote the internationalization of the university and its world-class advanced research. The AIMR has become the first member institute of this organization. Furthermore, Tohoku University will create a research reception center at the OAS by applying the accumulated knowledge of the AIMR. The AIMR and its researchers will play a central role in all these initiatives, leading Tohoku University in promoting research and globalization. I am particularly gratified by the fact that AIMR's experiences have become a driving force for promoting system reform and internationalization throughout the university. The reforms have created ripple effects across the university.

As for international partnerships in 2014, the AIMR established a joint research center with the University of Chicago (USA), expanding on its existing partnerships with the University of Cambridge (UK), the Institute of Chemistry at the Chinese Academy of Sciences (China) and the University of California, Santa Barbara (USA). Through these joint centers, we aim to develop a system that focuses on implementing research conducted together with leading materials-science research institutes. This year, we held joint workshops with the University of Chicago and the University of Cambridge. Moreover, the AIMR jointly organized a workshop with other WPI centers at the 2014 Spring Meeting of the European Materials Research Society, which was a great success.

In the eight years since its inauguration, the AIMR has generated many promising results. And we plan to further reinforce our global network with joint centers and

partner institutions, with the goal of forming a global community for promoting collaboration between mathematics and materials science. I would like to take this opportunity to thank you for your interest and hope that this publication will spark many more initiatives.

Motoko Kotani
Director
AIMR



Tohoku University's Advanced Institute for Materials Research (AIMR) promotes fusion research in materials science across disciplinary barriers

The AIMR is leading the world in facilitating collaboration between materials science and mathematics. In an environment where more than half of the researchers come from abroad, scientists at the AIMR — young and international included — contribute to discussions and joint research projects, enabling the AIMR to achieve world-leading research results.

AIM*Research*'s website introduces cutting-edge research from the AIMR through research highlights, spotlights, news and job vacancies. Access AIM*Research* online now!

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The AIMR advances research in bulk metallic glasses, materials physics, soft materials and devices/systems, and actively promotes collaboration among these divisions toward the development of groundbreaking technologies that cross the boundaries of conventional fields of study — bridging the disciplines of materials science, physics, chemistry and precision, mechanical, electronics and information engineering. The Mathematics Unit further complements the AIMR's research activities.

Tissue engineering

Strong hydrogel carries current

Supporting a hydrogel with a carbon-nanotube network helps to grow muscle tissue for medical applications

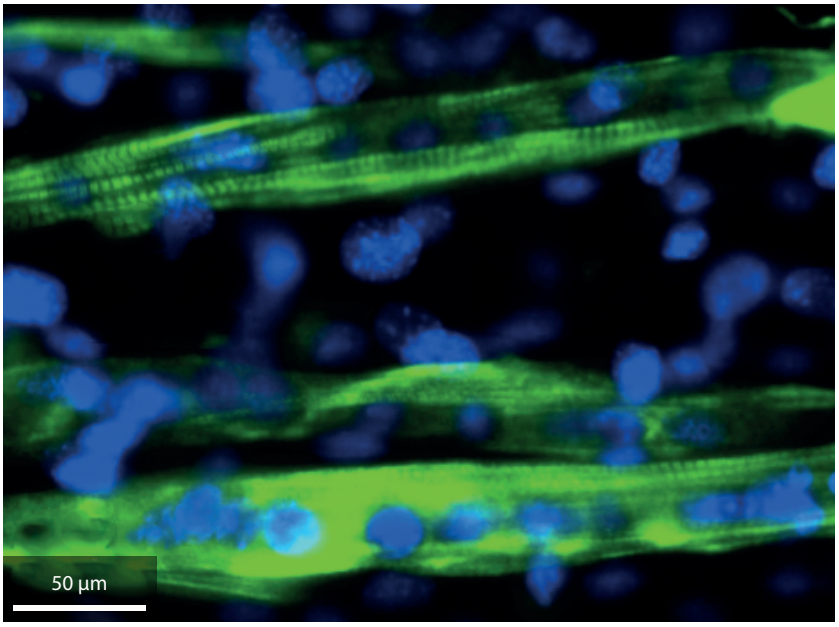
Cultured cells can form functional, three-dimensional tissue if given a suitable scaffold to guide their growth. Biocompatible hydrogels — which contain mostly water — provide useful scaffolds for some cell types. However, the usual method of stiffening hydrogels by reducing their water content can impede cell growth. In addition, hydrogels do not typically conduct electricity, making them unsuitable for cells that require electrical stimulation to grow.

Samad Ahadian and colleagues from the AIMR at Tohoku University have now used carbon nanotubes to create a hydrogel that is both sturdy and a good conductor of electricity[1]. The addition of nanotubes presents an alternative way to tune both the mechanical and electrical properties of hydrogels, the researchers say.

Using a gelatin methacrylate hydrogel as a base, the researchers added multi-walled carbon nanotubes — thin straws of carbon atoms measuring 40–90 nanometers in diameter — to double the hydrogel's stiffness.

Initially, the nanotubes were randomly oriented in the gel, but the researchers were able to align them by applying an electric field. Next, they used a burst of ultraviolet light to form bonds between the gelatin methacrylate molecules, fixing the nanotubes in place. The nanotube network enabled the gel to carry between 100 and 1,000 times more current than the unaligned nanotubes, depending on the nanotube concentration.

The researchers then tested their hydrogel as a growth medium for C2C12 mouse muscle myoblasts, a type of muscle cell that can fuse together to form myotubes. The myotubes in turn mature into myofibers, which behave like normal muscle tissue.



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Myoblasts (green) can fuse to form functional muscle fibers after aligning in grooves within a carbon-nanotube-supported hydrogel. Cell nuclei are stained in blue.

More than 95 per cent of the myoblasts seeded into the nanotube-laden gel survived. Additionally, after three days in culture the growth of the cells accelerated thanks to the greater number of anchoring sites offered by the nanotubes.

By creating a groove in the hydrogel, the researchers were able to encourage myoblasts to line up end-to-end, helping them to form healthy myotubes that could contract properly. After eight days in culture, the researchers applied a small voltage that promoted muscle cell differentiation along the groove — an effect that was most pronounced in the aligned-nanotube hydrogel (see image).

Hydrogel-grown muscle tissue has numerous potential medical applications. "Engineered muscle tissues can be used as an efficient platform to investigate drug candidates to treat diabetes," explains Ahadian. "Such tissues can be made using a patient's own muscle cells, which could be a major step toward personalized medicine and would make it possible to eliminate expensive and time-consuming animal experiments for drug screening."

1. Ramón-Azcón, J., Ahadian, S., Estili, M., Liang, X., Ostrovidov, S., Kaji, H., Shiku, H., Ramalingam, M., Nakajima, K., Sakka, Y. *et al.* Dielectrophoretically aligned carbon nanotubes to control electrical and mechanical properties of hydrogels to fabricate contractile muscle myofibers. *Advanced Materials* **25,** 4028–4034 (2013).

Solar cells

The benefits of separation

A better understanding of how electrical charges separate in organic solar cells is helping to improve energy harvesting

The plastic materials used in organic solar cells are abundant and cheap, making such devices promising for harvesting solar energy. The complexity of the organic molecules used in these cells, however, has prevented a full understanding of the mechanism by which they convert sunlight into electrical charge. This complexity has also hampered their use in practical applications. Hiroyuki Tamura and Irene Burghardt from the AIMR at Tohoku University and the Goethe University Frankfurt, Germany, respectively, have now shown how the distribution of electrons across an organic solar cell plays a crucial role in generating electricity[1].

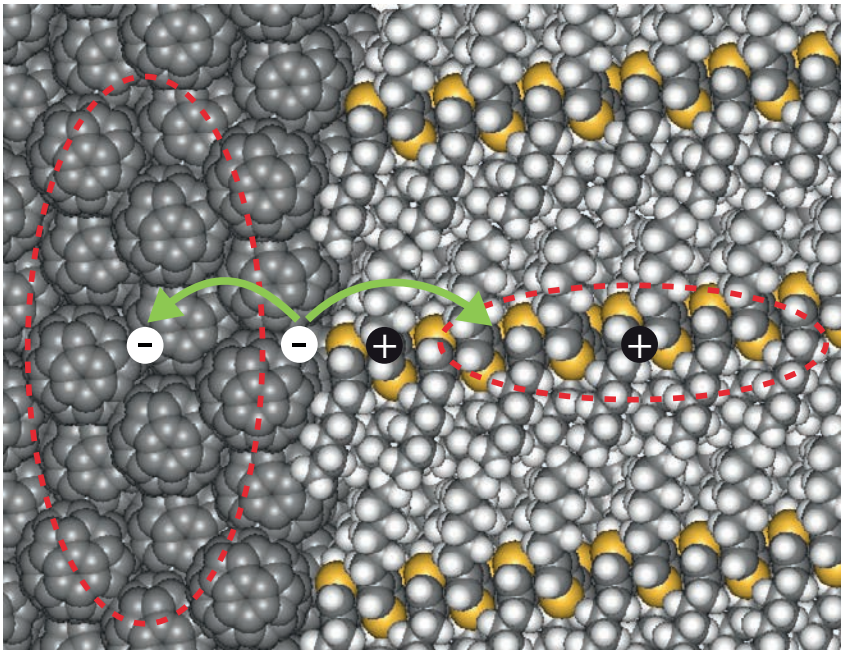
Organic solar cells are typically comprised of a mixture of polymer molecules and cage-like spherical balls of carbon known as 'buckyballs'. Light incident at the interface between these molecules excites the electrons present in the molecules. As the electrons move across the molecules, they leave behind empty spaces — 'holes' — which are also mobile. The role of the buckyballs is to transport the electrons away to the contact electrode while the polymers carry the corresponding holes (see image).

A crucial aspect for the operation of an organic solar cell is the initial charge separation of electrons from the polymer into the buckyballs. "A faster charge separation leads to a more efficient operation of the solar cell as it minimizes the opportunity for electrical losses," explains Tamura. However, the size and complexity of the organic molecules involved has impeded a deeper understanding of this process.

To investigate the charge-transfer mechanism, Tamura and Burghardt used powerful quantum dynamical simulations that were able to compute the properties of large systems. Their results reveal that the charge transfer is not initiated by the simple 'hopping' process of electrons from the polymers to the buckyballs.

Rather, the charge transfer relies on the fact that in quantum physics each electron can also be described as a wave, which is spread out in space. When an electron is excited by sunlight, its wavefunction expands. This expansion lowers the energy barrier for the charge-transfer process to occur, thus enabling the electrons to move to the buckyballs. "Unlike hopping processes, this scheme can explain the efficient, ultrafast charge-separation observed in some experiments," explains Tamura.

The new mechanism will be important for the design of enhanced organic solar cells. For example, adds Tamura, "the reduced energy barrier will allow solar cell designs that enable the absorption of a broader cross-section of sunlight, especially at longer wavelengths."



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Organic solar cell comprising buckyballs (left) and chains of polymer molecules (right). The separation of electrons (minus sign) and holes (plus sign) to opposite contacts of the cell is crucial for the efficient performance of the cell.

1. Tamura, H. & Burghardt, I. Ultrafast charge separation in organic photovoltaics enhanced by charge delocalization and vibronically hot exciton dissociation. *Journal of the American Chemical Society* **135,** 16364–16367 (2013).

Biomaterials

Carpeting the way for less-invasive treatments

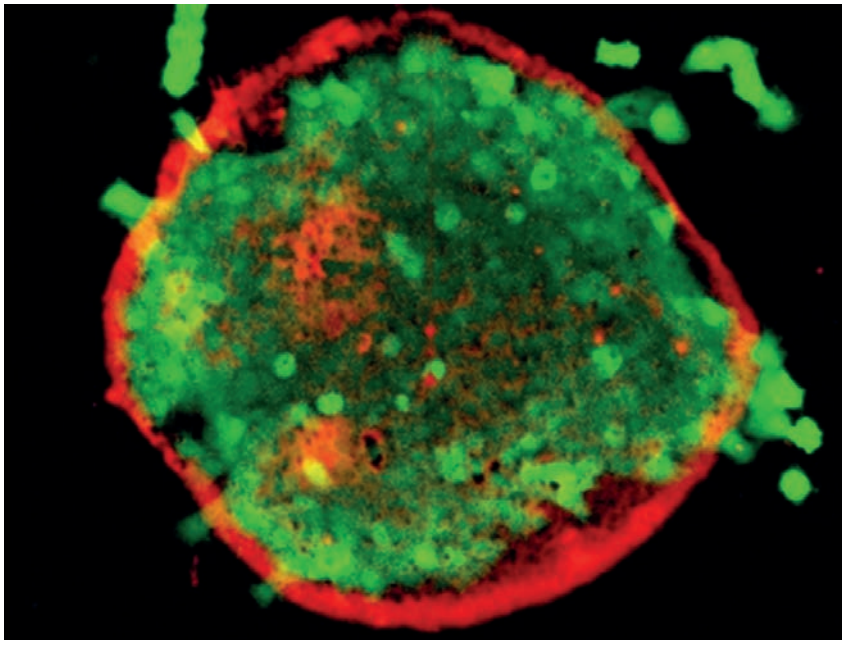
Ultrathin polymer-based sheets aid tissue repair by providing a new platform for targeted cell transplantation

Tissue engineering is expected to offer innovative regenerative approaches for cell organization and delivery in the body. A research team led by Toshinori Fujie and Ali Khademhosseini from the AIMR at Tohoku University has now developed ultrathin polymer sheets — 'nanosheets' — that support cell growth and transplantation at a specific location[1].

Fujie says that the team's nanosheets were inspired by the classical fairy tale "The Arabian Nights", in which a flying carpet delivers multiple people to desirable places. To manufacture the nanosheets, the team deposited the biodegradable polymer poly(lactic-*co*-glycolic) acid, together with magnetic nanoparticles to aid manipulation of the nanosheets, on a microscopic stamp. The researchers then transferred the micropatterned layer onto a glass surface pre-coated with a sacrificial polymer that, when dissolved in water, releases the nanosheet from the surface.

Fujie and Khademhosseini's team evaluated the potential for using their nanosheets to treat age-related macular degeneration — a common disease that leads to loss of sight and eventual blindness. Treatment of this disease hinges on repairing the damaged retinal pigment epithelium (RPE) layer of the eye, which is sandwiched between the retinal photoreceptors and the vascular network.

Using a syringe to transplant RPE cells at the degeneration site provides an attractive way to restore this damaged monolayer — the alternative approach is surgical intervention, which carries a high risk of infection. Materials scientists have already created several natural and artificial supports for delivery of the cells but their size exceeds that of the narrow subretinal space. Furthermore, the low flexibility of such supports hinders their aspiration and injection through a syringe.



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Monolayer of retinal pigment epithelium cells (green) on a polymer nanosheet (red).

In vitro assessments showed that RPE cells adhered to the team's nanosheets and self-assembled into a densely packed, cobblestone-like monolayer (see image). Moreover, the magnetic particles also enhanced the surface roughness of the nanosheets, thereby promoting cell migration and proliferation — a further advantage for RPE monolayer transplantation. When compressed in a syringe needle, the RPE-bearing nanosheets retained viable cells, whereas thicker sheets preserved only a few cells of mostly low viability. The nanosheets also recovered their original shape without distortion.

When injected into the subretinal space of a swine eye *ex vivo*, the nanosheets properly spread and attached to the macula. The RPE monolayer also retained its cellular activity during the procedure.

The researchers are currently investigating ways to utilize their nanosheets as scaffolds for stem cells and drug molecules. "The controlled release of drugs and growth factors from the nanosheets may enhance the tissue integration of the transplanted cells," says Fujie.

1. Fujie, T., Mori, Y., Ito, S., Nishizawa, M., Bae, H., Nagai, N., Onami, H., Abe, T., Khademhosseini, A. & Kaji, H. Micropatterned polymeric nanosheets for local delivery of an engineered epithelial monolayer. *Advanced Materials* **26,** 1699–1705 (2014).

Bioimaging

A sharper view of teeth

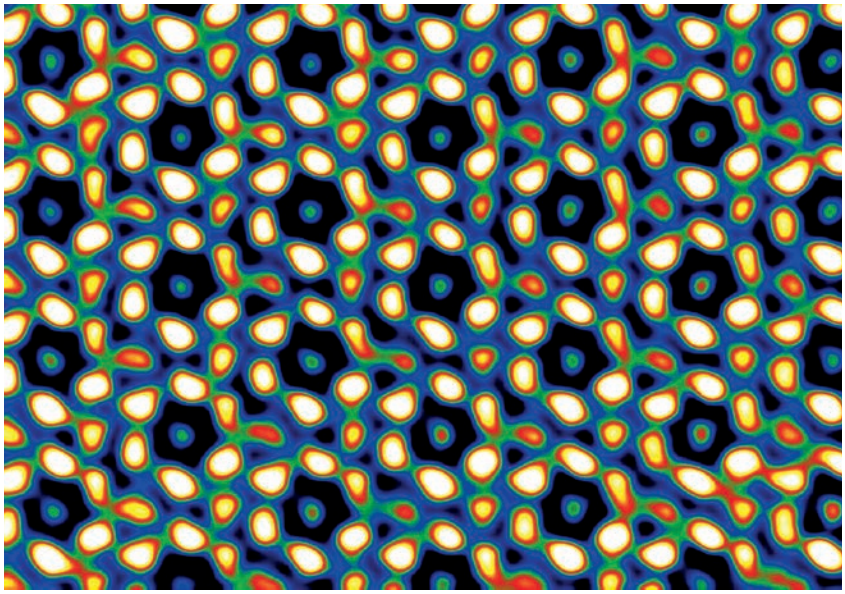
The first atom-resolved images of biominerals in shark teeth reveal important insights into fluorine's cavity-fighting power

Over the course of its lifetime, a typical shark will lose and regrow thousands of teeth as they become embedded in prey or worn out. None of these teeth, however, ever suffers from cavities. Recent studies have discovered that the hard, enamel-like coating of a shark tooth is made from fluorapatite — a fluorinated calcium phosphate material that is an active ingredient in most toothpastes. Although researchers already attribute high concentrations of fluoride ions to low levels of tooth decay, direct evidence of this chemical's cavity-reducing action remained elusive.

Chunlin Chen and colleagues from the AIMR at Tohoku University, in collaboration with researchers from across Japan, have now used transmission electron microscopy (TEM) to capture the first images of individual atoms inside shark teeth[1]. Their findings show that unusual bonding interactions between fluorine and calcium atoms may be critical to understanding fluorine's tooth-strengthening capabilities.

For decades, scientists have used TEM to observe the atomic-scale structure of inorganic materials. Shark teeth, however, are biominerals — complex substances containing both delicate organic matter and robust inorganic minerals, which are easily damaged by high-energy electron beams. Current understanding of the enamel-like structures that envelop shark teeth is thus limited to micrometer-sized regions.

To overcome this challenge, the researchers used a scanning transmission electron microscope equipped with special 'aberration-corrected' lenses and low-dose imaging capabilities. The approach employs a small lens aperture that disperses the electron beam over a wider area than usual, thereby lowering the beam intensity. However, because such a low-dose beam results in noisy TEM images, the researchers had to search for a careful balance between irradiation-induced damage and image quality.



© 2014 Chunlin Chen

Direct atomic imaging inside the enamel-like coating of a shark tooth shows that fluorine atoms (blue spheres) play a critical role in stabilizing tooth enamel.

When the team examined a tooth from an *Isurus oxyrinchus* — also known as a shortfin mako shark — TEM images showed that its enamel-like structure contained bundles of single-crystalline fluorapatite nanorods, roughly fifty nanometers wide. Deeper probing revealed a hexagonal atomic framework inside the nanorods, with calcium, phosphorus and oxygen surrounding a central fluorine atom (see image). This structure suggests that fluorine is critically important to shark tooth enamel as its loss would destabilize the entire chemical structure.

Computer simulations of the structure of fluorapatite further illustrated fluorine's unique role in dental health. The researchers were able to determine that bonding between fluorine and calcium contained both ionic and covalent contributions, making it stronger than typical fluorine bonds. "The direct imaging of fluorine atoms and its surprising mixed covalent–ionic bonding should be of fundamental significance to the field of dentistry," says Chen.

1. Chen, C., Wang, Z., Saito, M., Tohei, T., Takano, Y. & Ikuhara, Y. Fluorine in shark teeth: Its direct atomic-resolution imaging and strengthening function. *Angewandte Chemie International Edition* **53,** 1543–1547 (2014).

Catalysis

Pinning down degradation

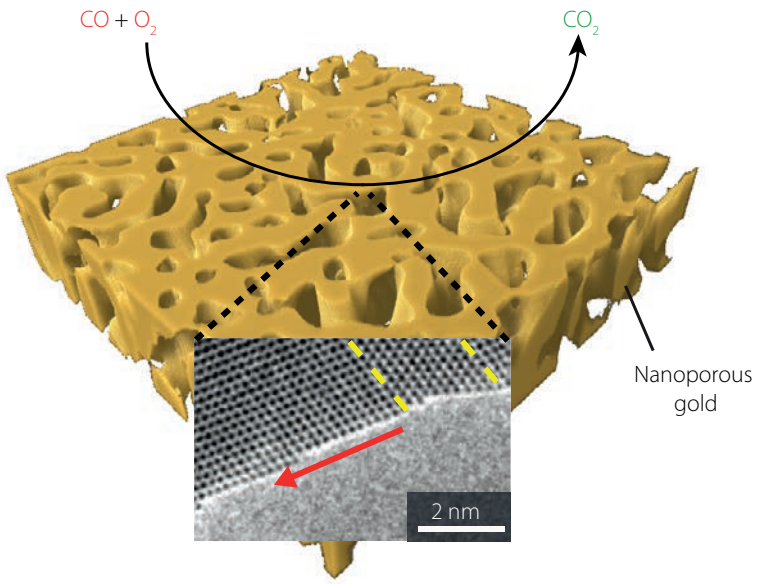
Atomic-scale examination of nanoporous gold demonstrates that surface defects suppress catalyst degradation during carbon monoxide oxidation

Nanoporous gold has a crucial role as a catalyst in the production and processing of commodity chemicals under environment-friendly conditions. Its tiny pores provide exceptional activity in reactions that involve oxygen, such as the thermodynamically challenging transformation of carbon monoxide (CO) into carbon dioxide. However, the mechanism that governs its degradation and loss of activity during catalysis has so far remained elusive.

By using sophisticated microscopy techniques to monitor changes in the structure of nanoporous gold during CO oxidation, a team led by Takeshi Fujita from the AIMR at Tohoku University has gained unprecedented experimental insight into the catalysis-induced degradation mechanism at the atomic scale[1]. Their work has also revealed the significance of planar defects — and in particular the formation of twin boundaries — in averting this process, thereby offering new avenues for enhancing catalytic activity and stability.

The researchers first synthesized freestanding nanoporous gold leaves through a dealloying process, in which nitric acid removes the silver from an ultrathin gold–silver sheet. The resulting gold structure comprised nanopores embedded in flat, close-packed 'terraces' separated by single-atom 'steps'.

The nanoporous gold catalyst did not exhibit any noticeable change under electron beam irradiation in pure CO or oxygen environments or under vacuum, indicating its stability. Upon exposure to a CO–air gas mixture, the nanopores and connecting material expanded with increasing reaction time, which was associated with a reduction in catalytic activity. Furthermore, silver and gold in the connecting material were initially uniformly distributed but gradually became separated as the reaction progressed.



Foreground: Modified from Ref. 1 © 2014 American Chemical Society; background: © 2014 Takeshi Fujita

Gold atoms migrate at right angles (red arrow) to a planar 'twin' interface (yellow lines) during the oxidation of carbon monoxide on nanoporous gold.

To gain insight into this coarsening mechanism, Fujita and colleagues used an environmental transmission electron microscope to obtain high-resolution images of individual nanopores under reaction conditions. When they increased the reaction time, the nearly round nanopores became faceted and widened before merging with neighboring pores.

The researchers found that the coarsening relied on the rapid oxidation-induced migration of gold atoms on the single-atom reactive steps of the uppermost terrace (see image). The nanopores grew fastest perpendicular to the twin interfaces — a clear indication of the importance of these defects. In the absence of twin defects, the nanopores did not display any preference in growth direction. "Twin planes can effectively pin the gold atoms to the surface, eventually suppressing nanopore coarsening," explains Fujita.

The team is currently evaluating ways to boost catalyst performance and longevity by augmenting the density of planar defects in nanoporous gold. "We are also trying to develop new exhaust gas catalysts based on this system," adds Fujita.

1. Fujita, T., Tokunaga, T., Zhang, L., Li, D., Chen, L., Arai, S., Yamamoto, Y., Hirata, A., Tanaka, N., Ding, Y. & Chen, M. Atomic observation of catalysis-induced nanopore coarsening of nanoporous gold. *Nano Letters* **14,** 1172–1177 (2014).

Materials

Polymer chains singled out

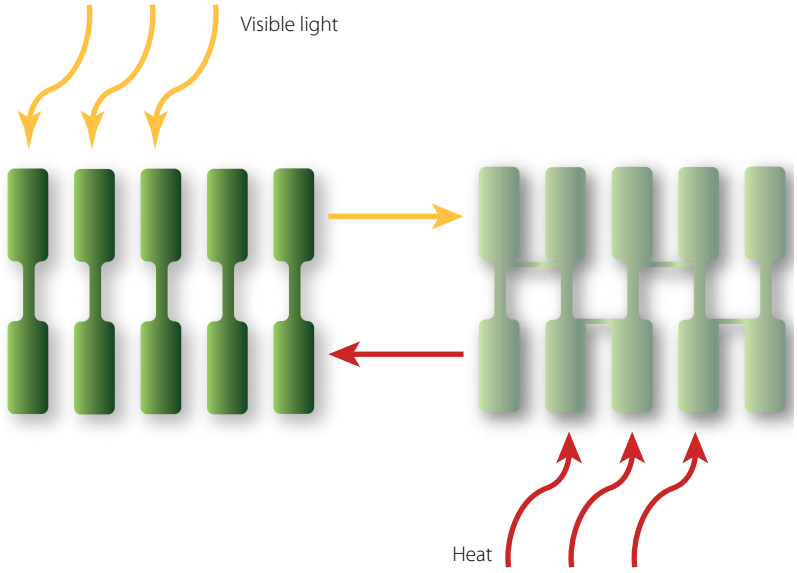
Colorless single-polymer chains can be made from colorful dye monomers held rigid inside a molecular crystal

Single crystals of polymers can be difficult to obtain because their long and flexible backbones tend to get tangled, forming structures with no long-range order. However, the process of preparing these polymers is eased if polymerization takes place inside a molecular crystal in which the reactive monomers are pre-organized in a position that almost corresponds with the repeat distance of the desired polymer. The confinement of these monomers during polymerization yields long single-polymer chains.

Researchers from the AIMR at Tohoku University and the University of California have used this approach to synthesize a new class of polymers[1]. They constructed two new polymers from bis(indenedione) monomers, which are highly colored conjugated organic dyes.

Polymerization ordinarily requires heat, ultraviolet light or pressure. In contrast, the researchers used visible light to induce the reactions between the monomers and produce the new polymers (see image). "This is the first time that the quantitative conversion of a small molecule to a macromolecule has been achieved with visible light," says Yonghao Zheng, a member of the research team.

Unlike the monomers they were constructed from, the polymer strands are colorless because polymerization breaks the monomers' conjugation. The progress of the reaction can therefore be seen with the naked eye. The researchers shone light on the molecular crystal, causing the top layer of the crystal to polymerize and become transparent. Light can then pass through to the next layer, which subsequently undergoes polymerization. This continues until the entire crystal is colorless. The researchers were able to isolate individual polymer strands by applying and then removing sticky tape from the polymerized crystal.



© 2014 Yonghao Zheng

Visible light causes the monomers in the molecular crystal (green) to polymerize, a reaction that can be reversed by heating.

The resulting polymers are strong, explains Zheng. "One possible application is as a strengthening component in composite materials." The polymers lose their translucency when heat is applied, breaking them down to their component parts, which allows any weaknesses to be spotted.

The researchers also showed that single chains of the two polymers could be made inside molecular crystals dissolved in highly concentrated solutions, as well as on semicrystalline thin films. These synthetic methods are well-suited to manufacturing, thereby opening up this class of polymers to a wide range of applications. "The feature of polymerization on thin films is of great potential for solution-processing applications in organic electronics, such as thin-film transistors," says Zheng.

The researchers now plan to focus on unfolding the fundamental properties of single chains of polymers and are currently studying their mechanical properties.

1. Dou, L., Zheng, Y., Shen, X., Wu, G., Fields, K., Hsu, W.-C., Zhou, H., Yang, Y. & Wudl, F. Single-crystal linear polymers through visible light–triggered topochemical quantitative polymerization. *Science* **343,** 272–277 (2014).

Oxide interfaces

Blueprint for a super-material

Atomic-scale images expose the secret mechanisms that turn insulating oxide films into electrically and magnetically active interfaces

Metal oxides play many important roles across a variety of high-tech energy applications, such as photovoltaic cells and lithium-ion batteries. Recently, scientists discovered that the electronic properties of extremely thin metal oxide films are unlike those of any other material. Developing metal oxide thin films into practical devices requires atomic-level knowledge of their structures and properties. Unfortunately, the complex chemical arrangement of such films makes them difficult to characterize using standard techniques.

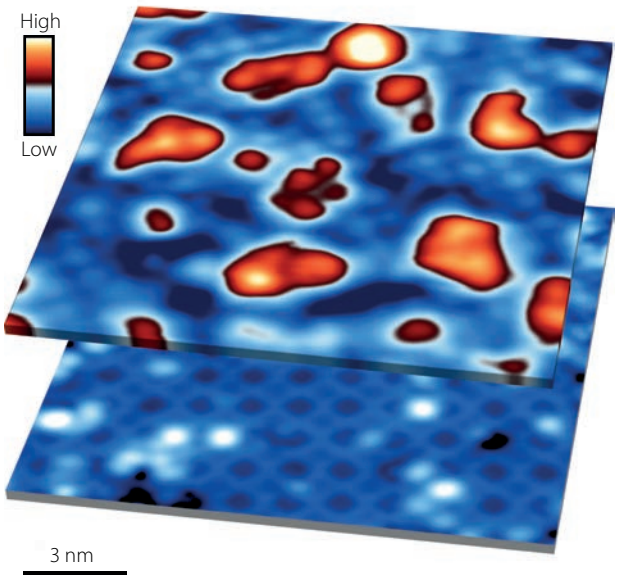
Takeo Ohsawa, Taro Hitosugi and colleagues from the AIMR at Tohoku University have now used scanning tunneling microscopy to visualize atoms inside metal oxide thin films[1]. This approach provided the researchers with unprecedented surface images of strontium titanate ($SrTiO_3$) — an insulating metal oxide that transforms into a two-dimensional conductor, a magnet or even a superconductor when interfaced with lanthanum aluminate ($LaAlO_3$).

According to Ohsawa, many aspects of this $LaAlO_3/SrTiO_3$ system are controversial — particularly a phenomenon known as the 'termination layer' problem. $SrTiO_3$ is made of alternating sheets of titanium dioxide (TiO_2) and strontium oxide (SrO), which means that it exhibits contrasting effects, depending on which layer is in contact with $LaAlO_3$. Films terminating with TiO_2 become two-dimensional conductors, whereas those terminating with SrO retain their insulating properties.

To investigate this problem, the researchers combined a low-temperature scanning tunneling microscope with a laser-driven, thin-film deposition system. This allowed them to observe the early stages of SrO film growth — a critical period during the establishment of a new material. First, they prepared an ultra-clean $SrTiO_3$ surface terminated by a periodically arranged layer of titanium and oxygen atoms. Then they used the scanning tunneling microscope to monitor how the surface changed as a pulsed laser slowly deposited increasing amounts of SrO.

Instead of forming crystalline structures, the SrO atoms clumped together into random, 'island'-type arrangements (SrO_x) that disrupted the periodicity of the underlying titanium–oxygen layer (see image). Careful comparisons of pre- and post-deposition surfaces revealed that titanium atoms merged with the SrO_x islands during this growth phase, thus forming an atomic mixture that can disrupt interfacial electron transport.

"These results indicate the possibility of titanium atom incorporation into $LaAlO_3$ films when they are deposited on SrO-terminated $SrTiO_3$ substrates, which may lead to the suppression of two-dimensional conductivity in this system," says Ohsawa. The researchers say that the need to account for excess titanium at the $LaAlO_3/SrTiO_3$ interface should help to solve the termination layer problem, while also giving researchers a blueprint for developing atom-by-atom engineered oxides with exotic electronic properties.



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Scanning tunneling microscopy images of strontium oxide (SrO_x) islands (red, top) after deposition of SrO on a titanium–oxygen surface (bottom).

1. Ohsawa, T., Shimizu, R., Iwaya, K. & Hitosugi, T. Visualizing atomistic formation process of SrO_x thin films on $SrTiO_3$. *ACS Nano* **8,** 2223–2229 (2014).

Material defects

Down to the core

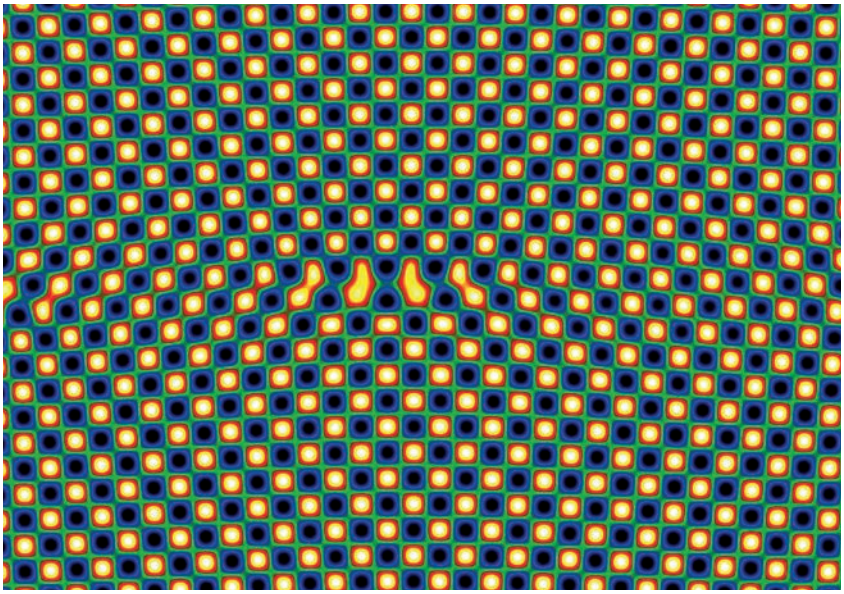
Crystal defect cores adopt multiple arrangements in real materials

Crystal dislocations play a crucial role in defining the physicochemical properties of many materials. These linear defects, although capable of causing structural failure in semiconductor-based devices, contribute significantly to the plastic behavior of metals and alloys. However, the core structures of such defects remain poorly understood.

A team of researchers led by Yuichi Ikuhara from the AIMR at Tohoku University have now uncovered the structures of dislocation cores at the atomic scale[1]. "Different dislocation cores can have a vastly different impact on the properties of real materials," explains Zhongchang Wang. The researchers investigated these structures by combining complex simulations of atoms with systematic, high-resolution imaging.

Existing attempts to characterize dislocation cores have relied on either diffraction or scanning transmission electron microscopy (STEM). Diffraction provides only averaged structural information and is thus unable to detect individual defects. STEM, on the other hand, enables atomic resolution imaging but is limited to just a few dislocations. "Unless the total number of dislocation types in the material is known, we can only observe a selection of individual defects in the sea of dislocations in a real material," says Wang.

Using a computational–experimental approach, the researchers determined the geometrical arrangements of all dislocation core structures for each dislocation type. First, they generated bicrystals from magnesium oxide (MgO), an ionic material that exhibits dislocation-dependent properties. Then, they joined two identical MgO crystals at a slight angle to create one-dimensional edge dislocations. An extensive computational search provided optimal dislocation structures, which the researchers then compared with electron microscopy images.



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The atomic arrangement at the [100] dislocation of magnesium oxide. This arrangement differs from that in the bulk, which may result in dramatically different material properties.

The team's investigations showed that only one stable structure exists for the [110] dislocation of MgO — a finding that is consistent with previous observations. Atom-resolved STEM imaging gave the same core structure as the computed geometry for this dislocation, thus validating the researchers' approach. Further simulations revealed three core arrangements with similar energies for the [100] dislocation (see image), which matched the electron microscopy images.

"Impurities preferably segregate at [100] dislocations instead of at [110] dislocations in MgO, which may explain why the presence of [100] dislocations damages the intrinsic insulating properties of MgO whereas the [110] dislocation is not detrimental to MgO electronic devices," explains Wang. "We are now applying this technique to investigate dislocation core structures in other materials, such as TiO_2," says Ikuhara. In addition, the researchers are also planning to determine the differences between cores by measuring the properties of individual dislocations.

1. Wang, Z., Saito, M., McKenna K. P. & Ikuhara, Y. Polymorphism of dislocation core structures at the atomic scale. *Nature Communications* **5,** 3239 (2014).

Nanomaterials

Tiny flakes with a brilliant future

Newly discovered atomic sheets could outshine graphene in photosensitive detectors

Graphene — an ultrathin material consisting of a single layer of carbon atoms — has the potential to revolutionize electronic devices by making them smaller, faster and more efficient. One limitation of graphene, however, is that it can absorb only a small fraction of visible light. This prevents it from being used in photodetectors — optoelectronic components critical to the operation of solar cells and digital cameras.

Katsumi Tanigaki and colleagues from the AIMR at Tohoku University have now discovered a novel nanostructured material — gallium telluride (GaTe) flakes — that can detect light signals with a higher sensitivity and a faster electrical response than any existing two-dimensional (2D) layered material[1].

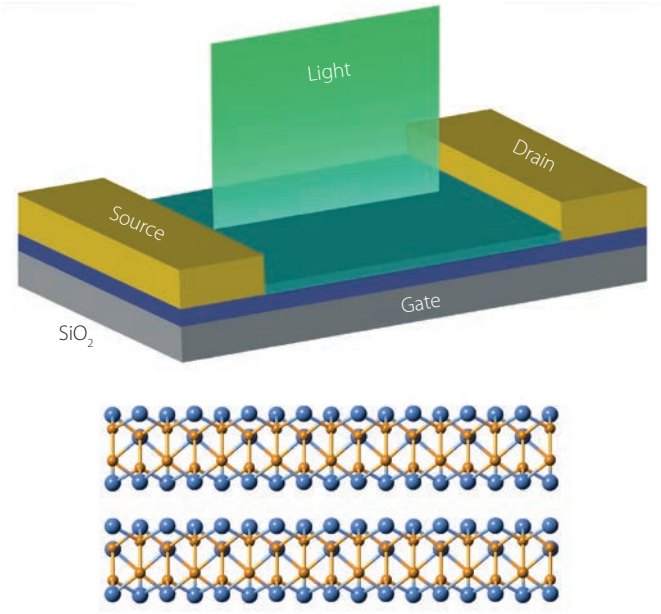
Although electrons can move through the hexagonally bonded framework of graphene at extraordinary speeds, graphene's 'indirect' optical bandgap means that any interaction with light must proceed via a time- and energy-consuming detour involving intermediate states. 'Direct' bandgap materials, in contrast, can absorb large quantities of photons by immediately converting them into a photoelectric current, making such materials extremely photosensitive.

The researchers' extensive search for a direct-bandgap material that is atomically thin led them to GaTe crystals. This material's unique structure — 2D sheets of Te–Ga–Ga–Te atoms (see image) stacked into weakly bonded, multilayered complexes — provides it with intriguing optoelectronic properties. Furthermore, GaTe is lightweight and easy to synthesize.

But when the researchers began their investigation, they encountered a crucial problem: the bandgap of GaTe changes from being direct to indirect when its bulk crystal structure is thinned down to a monolayer. Through collaboration with theoreticians from the United Kingdom to better understand the optical properties of this system, the team came to realize that finite, ten-layer GaTe stacks could yield the improved conductivity of 2D systems while retaining a direct bandgap.

To achieve this goal, the researchers resorted to a low-tech but effective method: using sticky Scotch tape to strip off very thin flakes from bulk GaTe crystals. This technique — pioneered for isolating single-layer graphene — produced the desired multilayered GaTe flakes, which they then transferred to a silicon device. Experiments showed that the tiny flakes could respond to a wide range of light within milliseconds. Importantly, the nanomaterials produced a photocurrent of light-generated electrons several orders of magnitude higher than that generated by graphene.

"A direct bandgap is very important for achieving both a high sensitivity and a fast response time in a photodetector," says Tanigaki. "The intrinsic direct bandgap available from GaTe nanoflakes makes them a promising candidate for future photodetectors beyond graphene."



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A novel sensor based on two-dimensional gallium telluride (GaTe) sheets is extremely sensitive to light signals.

1. Liu, F., Shimotani, H., Shang, H., Kanagasekaran, T., Zólyomi, V., Drummond, N., Fal'ko, V. I. & Tanigaki, K. High-sensitivity photodetectors based on multilayer GaTe flakes. *ACS Nano* **8**, 752–760 (2014).

Nanodevices

Molecular motor powers shuttle

Kinesin protein ferries microtubules along nanotube track

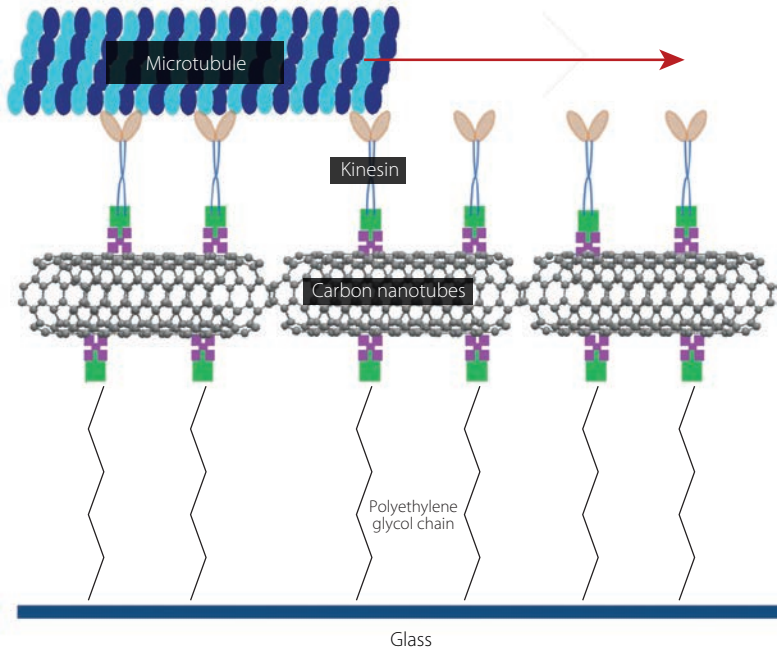
Miniature chemical reactors, known as lab-on-a-chip devices, are increasingly being used to analyze biological samples. Unfortunately, the bulky pumps and batteries needed to operate such devices limit their further miniaturization and prevent them from being directly implanted into the body for monitoring applications.

Winfried Teizer from the AIMR at Tohoku University and colleagues have now developed a much smaller system that uses a biological motor to transport cargo along a track made of carbon nanotubes (see image)[1].

Kinesin-1 is a natural motor protein that is powered by adenosine triphosphate (ATP), the principal energy-carrying molecule in cells. Kinesin uses this energy to carry cell components along hollow cylinders called microtubules, which consist of polymers of tubulin proteins and are typically 25 nanometers wide and several micrometers long. Teizer's team reversed this arrangement by anchoring kinesin proteins along a track, and then using them to propel microtubules like a conveyor belt.

The researchers coated a glass plate with aminosilane molecules and attached them to polyethylene glycol chains tipped with a biological compound called biotin. They then added multiwalled carbon nanotubes (MWCNTs) that were peppered with streptavidin, a protein that binds strongly to biotin. The streptavidin molecules covered the nanotube surface with a density of around 35,000 per square micrometer.

The scientists used electrodes that were crenellated into a saw-tooth pattern to subject the nanotubes to an electric field. This process, called dielectrophoresis, neatly aligned the nanotubes so that they formed tracks between the electrodes.



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Multiwalled carbon nanotubes attached to a glass plate act as a track for a kinesin-powered microtubule conveyor belt.

The researchers covered the nanotubes with kinesin bearing a biotin linker, and then added microtubules that had been labeled with a fluorescent dye called rhodamine. As the kinesin molecules consumed ATP, they forced the microtubules to glide along the track at an average speed of around 150 nanometers per second. This is slower than kinesin's usual velocity of about 800 nanometers per second. The researchers suggest this may be because their kinesin was engineered to be shorter than natural kinesin, limiting its ability to twist as it propels the microtubules.

"We have demonstrated that gliding on MWCNTs is possible, but we don't know if the microtubule shuttle can transit between tracks, which would allow the possibility of a complete circuit based on MWCNTs," says Teizer. "We are now investigating microtubule displacement between MWCNT segments."

The researchers hope that their microtubule conveyor belt could eventually be loaded with cargos such as viruses, drugs, proteins or nanoparticles, which would be useful for a variety of biosensing applications.

1. Sikora, A., Ramoń-Azcoń, J., Kim, K., Reaves, K., Nakazawa, H., Umetsu, M., Kumagai, H., Adschiri, T., Shiku, H. & Matsue, T. *et al.* Molecular motor-powered shuttles along multi-walled carbon nanotube tracks. *Nano Letters* **14,** 876–881 (2014).

Nanoparticles

Stretching water droplets

Water droplets suspended within oil have been pulled into stable, elongated shapes

Droplets of water suspended in oil are spherical because this shape minimizes the contact area between these two immiscible liquids. Researchers from the AIMR at Tohoku University and the University of Massachusetts in the United States have now used nanoparticles to modify the shape of liquid drops suspended inside another liquid[1]. The drops retain their modified shapes for long periods of time. "This is the first demonstration of stable, long-lived, non-equilibrium shapes of one fluid inside another," explains team leader Thomas Russell.

The researchers added the nanoparticles to a dispersion of water and an amine-ended polymer in oil. The polymers initially congregated at the interface between the oil and water. The nanoparticles then diffused from the aqueous phase to the interface, where they interacted with the amine groups of the polymer to form nanoparticle surfactants. These grouped together to minimize the surface tension at the interface.

Next, the researchers placed the system between two electrodes and applied an electric field. Electrostatic forces induced by the electric field caused the drops to deform and elongate into ellipsoids (see image). The surface area of each drop increased substantially while the drop volume remained constant, thus allowing more nanoparticle surfactants to form at the interface.

The extent to which the drops elongate depends on the strength of the applied electric field. When the researchers turned the electric field off, each drop tried to return to its original spherical shape. Although the drops did relax slightly, any significant decrease in surface area was prevented by the nanoparticle surfactants being grouped together at the interface. The team investigated a series of different groupings by changing the direction of the electric field, thereby creating a range of shapes. They also deformed the drops by stirring, thus forming tubules of water in the oil phase.

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Spherical water drops suspended in oil and coated in nanoparticle surfactants can be stretched into elliptical shapes by applying an electric field.

The drops retained their non-spherical shapes for at least a month. "Eventually the liquid within the droplet diffuses into the outer liquid and evaporates, causing the nanoparticle assembly to wrinkle," explains Russell. In their wrinkled form, the droplets resemble raisins in appearance.

This work could help realize the dream of all-liquid batteries. "If one liquid is an insulating oil and the second is aqueous based, we can transport charge quickly within the aqueous phase from one side of a container to another," says Russell. "This is precisely what is needed for battery applications; our work presents a route by which an all-liquid battery could be produced."

1. Cui, M., Emrick, T. & Russell, T. P. Stabilizing liquid drops in nonequilibrium shapes by the interfacial jamming of nanoparticles. *Science* **342,** 460–463 (2013).

Spintronics

Tuning materials for improved memory performance

Material composition tuning is moving magnetic tunnel junctions closer to reality

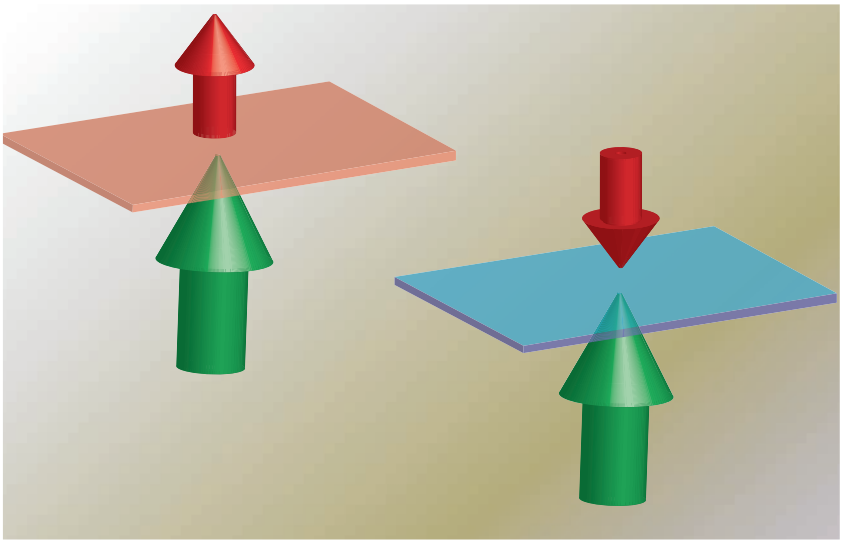
Today's magnetic storage media tend to orient their bits vertically — that is, perpendicular to the thin films that carry them. This arrangement, known as perpendicular magnetic anisotropy, has several advantages over older techniques: it not only lowers the electrical current needed to switch the direction of the bit (and therefore to write information) but also makes the bit more thermally stable.

However, there are some difficulties in using perpendicular magnetic anisotropy. One is the relative difficulty of controlling the magnetic interaction between adjacent films, which is necessary for emerging technologies like spin valves and all-optical data storage. In particular, an antiferromagnetic arrangement, in which the magnetic dipoles of adjacent films point in opposite directions, is difficult to achieve. Now, Qinli Ma and co-workers in the Mizukami Laboratory at the AIMR at Tohoku University have demonstrated a new way of controlling the interaction between adjacent magnetic layers that allows the creation of ferromagnetic or antiferromagnetic arrangements at will[1].

The researchers fabricated an interface between two magnetic thin films — one made from manganese and gallium and the other made from iron and cobalt — in which the magnetic bits were defined perpendicular to the films' plane (see image). As they increased the cobalt content of the iron–cobalt film beyond 25 per cent, the interface between the films abruptly switched from ferromagnetic (with aligned dipoles) to antiferromagnetic.

Ma and co-workers say that this unusual behavior results from the energy structure of their two films. The behavior of the film interface is dominated by the highest-energy electrons in each film. Increasing the cobalt content adds electrons to the iron–cobalt film, thus raising the energy of the highest-energy electrons at the interface. Because the number of available electron states that align antiferromagnetically is greater at higher energies, the film interface switches from ferromagnetic to antiferromagnetic when enough cobalt is added.

Using variations in the density of states to tune the behavior of an interface may prove to be an important new tool in engineering thin-film magnetic systems, says Ma. It also improves the prospects for the use of manganese–gallium films in applications like magnetic random-access memory. In fact, when the researchers used their pair of films to build a memory device called a magnetic tunnel junction, the device performed unusually well. They were able to vary the device's resistance by 60 per cent at room temperature using magnetic fields alone and by 120 per cent at low temperature, suggesting that practical devices may not be far off.



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At low cobalt concentrations (left), the spin in the iron–cobalt film (red arrow) is aligned with the spin in the manganese–gallium film (green arrow) by ferromagnetic exchange interaction at the interface (red sheet). As the cobalt content is increased (right), the iron–cobalt film spin flips to oppose the spin in the manganese–gallium film by antiferromagnetic exchange interaction at the interface (blue sheet).

1. Ma, Q. L., Mizukami, S., Kubota, T., Zhang, X. M., Ando, Y. & Miyazaki, T. Abrupt transition from ferromagnetic to antiferromagnetic of interfacial exchange in perpendicularly magnetized $L1_0$-MnGa/FeCo tuned by Fermi level position. *Physical Review Letters* **112,** 157202 (2014).

Nanomaterials

Graphene grows up

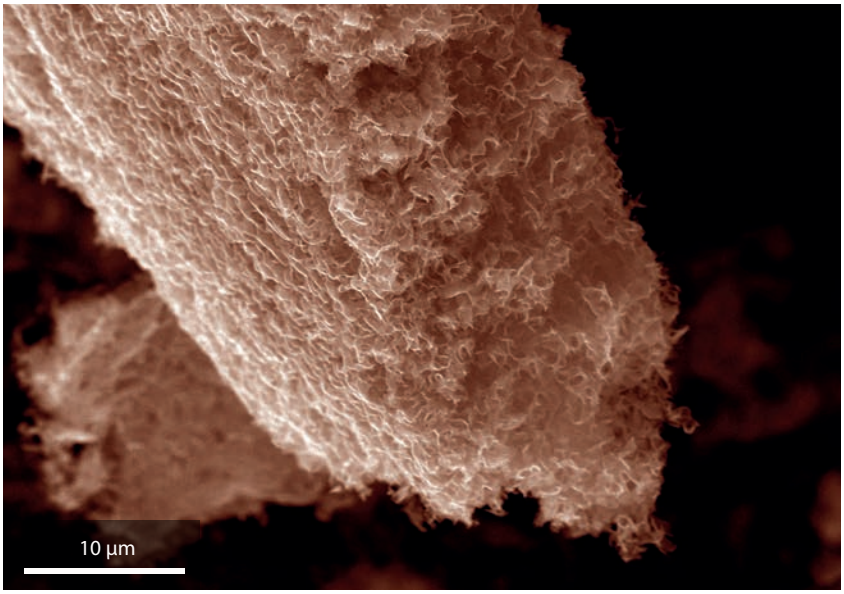
An innovative synthesis technique generates three-dimensional nanoporous graphene structures with high-speed electronic transport capabilities

The perfect, honeycomb-like bonding inside a sheet of graphene allows charge carriers to move through the material as 'massless' particles called Dirac fermions. This phenomenon gives graphene intrinsically higher electron mobility than any other known material — a feature that promises to usher in an age of ultrafast and inexpensive carbon-based electronics. However, the atom-scale thinness that makes graphene so valuable also makes it difficult to manipulate into practical devices.

Yoshikazu Ito, Mingwei Chen and colleagues from the AIMR at Tohoku University have now discovered a way to produce three-dimensional (3D) nanoporous graphene structures that preserve the massless Dirac fermions — and thus the astonishing electron mobility — of two-dimensional (2D) systems[1].

Turning graphene sheets into complex 3D networks is no easy task. A recently developed method, known as template-assisted growth, uses removable substrates to force carbon atoms into unconventional arrangements. This technique has successfully produced 3D graphene with intriguing mechanical and chemical properties. Yet the electrons inside these materials cannot travel efficiently because most templates have discontinuous or rough surfaces that introduce critical defects into the 3D framework.

The researchers developed an improved template with a 'bicontinuous' structure containing a smooth, hard surface of nickel atoms and nanoscale pores. Then, by carefully heating this template in a chemical vapor deposition (CVD) chamber filled with hydrogen, argon and benzene gases, they grew uniform films of graphene all over the nickel template.



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A scanning electron microscopy image of three-dimensional nanoporous graphene, a new low-cost material with extraordinary electronic properties.

Finally, they used acid to remove the nickel, yielding a freestanding, bicontinuous 3D structure of graphene with nanopores (see image).

Experiments revealed that the presence of the 3D nanopores, which the researchers could tailor by controlling the duration and temperature of the CVD process, had an enormous effect on graphene's electron transport properties. The bicontinuous structure reduced the frequency of geometric defects that naturally appear when flat, hexagonally bonded sheets are formed into 3D shapes, thus helping to retain graphene's 2D electronic character. 3D graphene with a large range of pore sizes behaved as high-speed quantum semiconductors, and the random orientations of the graphene sheets eliminated angular-dependent effects that often limit 3D device applications.

Ito explains that 3D nanoporous graphene has particular advantages over other graphene-based devices. "This material has abundant pore space for detecting molecules and promoting chemical reactions, in addition to its high charge mobility for applications in electronic devices," he says. "We expect it could create a low-cost and ecofriendly alternative to gas sensors, transistors or energy-harvesting devices such as lithium–air batteries."

1. Ito, Y., Tanabe, Y., Qiu, H.-J., Sugawara, K., Heguri, S., Tu, N. H., Huynh, K. K., Fujita, T., Takahashi, T., Tanigaki, K. & Chen. M. High-quality three-dimensional nanoporous graphene. *Angewandte Chemie International Edition* **53,** 4822–4826 (2014).

Nanomaterials

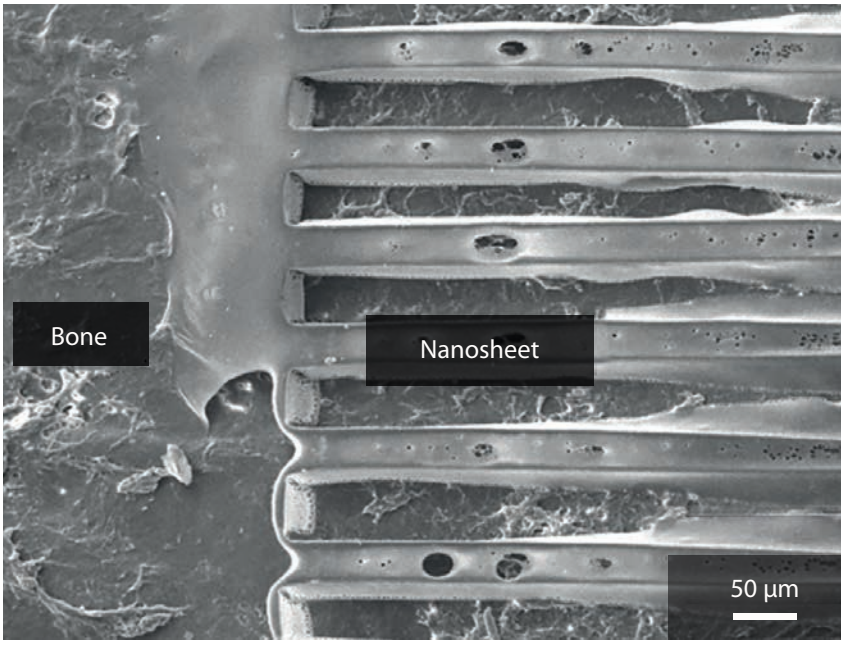
Building bone

Microgrooved polymeric nanosheets stuck to bone implants show promise for improved bone regeneration and repair

The surfaces of bones are often covered with a thin membrane, which is known as the periosteum. As well as providing mechanical strength and support, the periosteum is actively involved in the regeneration of injured bones. Osteoblasts — the major cellular component of bone — are produced by the differentiation of stem cells residing in this membrane. However, tissue engineering strategies for bone repair rarely consider this component of bone.

Inspired by the microstructure of the periosteum, Xuetao Shi and co-workers from the AIMR at Tohoku University and other institutions from around the world have fabricated an artificial periosteum by using patterned polymeric nanosheets[1]. This material is suitable for use in bone repair therapies. Natural periosteum consists of longitudinally oriented cells and collagen fibers, and the researchers mimicked this topography by fabricating nanosheets of poly(lactic-co-glycolic acid), or PLGA, which contain grooves with a spacing of about 50 micrometers.

Shi and his colleagues were able to noncovalently anchor the PLGA nanosheets to a variety of materials related to bone and bone repair, including a chicken wing bone, titanium alloy implants, and macroporous and microporous bioceramic tissue engineering scaffolds (see image). Promisingly, the researchers found that their nanosheets were difficult to detach from these surfaces. Furthermore, fluorescence microscopy revealed that the grooves in the nanosheets were preserved even after the sheets had adhered to bone or bone scaffolds — something that is important for correctly aligning stem cells.



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A microgrooved nanosheet adhered to the surface of a bone.

To test whether the PLGA nanosheets would be suitable for stimulating bone regeneration, the team seeded human mesenchymal stem cells capable of differentiating into bone onto the artificial periosteum. When they did this, they found that the stem cells aligned themselves in a parallel orientation to the grooves.

"The results indicate that the artificial periosteum not only acts a reservoir of stem cells for bone regeneration, but also controls the number of stem cells that become bone cells," explains Shi. Moreover, the microgrooved patterns on the nanosheets help direct protein and gene expression levels of the cultured cells in a similar way to natural periosteum, which is important for achieving effective bone repair.

The researchers are now planning to investigate the bone-generating properties of stem cells on the microgrooved nanosheets in animals. They expect that when the PLGA nanosheets are adhered to porous, tissue-engineering scaffolds, the nanosheets will degrade over the course of a month — a sufficiently long period for the stem cells to correctly align and differentiate into osteoblasts.

1. Shi, X., Fujie, T., Saito, A., Takeoka, S., Hou, Y., Shu, Y., Chen, M., Wu, H. & Khademhosseini, A. Periosteum-mimetic structures made from freestanding microgrooved nanosheets. *Advanced Materials* **26,** 3290–3296 (2014).

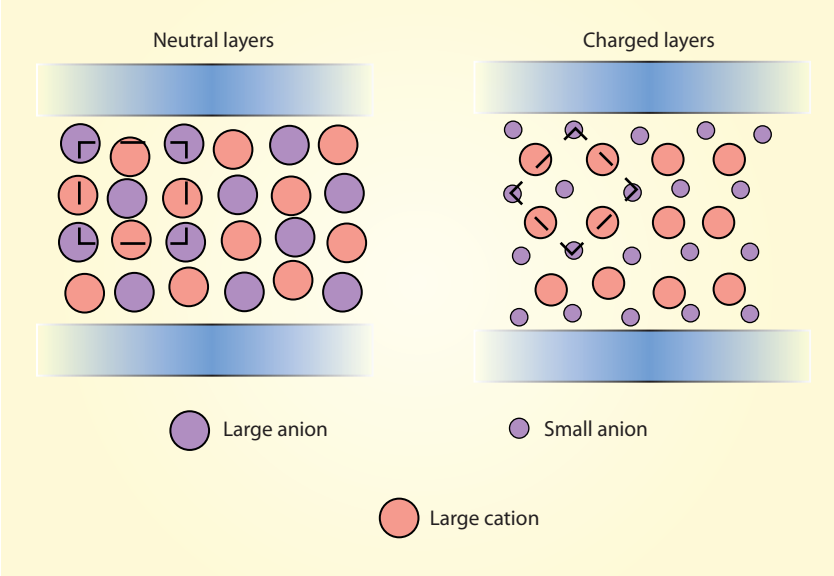
Ionic liquids

Going with the flow

Molecular models offer new insight into the flow of ionic liquids in confined spaces

Ionic liquids are environmentally friendly molten salts whose properties can be fine-tuned by carefully selecting their composite anion and cation molecules. In some cases, they exhibit extremely low friction when confined between two surfaces, making them candidates for replacing conventional lubricants in many applications. To advance their development and commercialization, it is vital to understand the molecular origin of their lubrication properties.

Now, Filippo Federici and colleagues from the AIMR at Tohoku University have theoretically investigated the behavior of the molecules in ionic liquids confined between two silica surfaces[1]. "Our study explores the relationship between the molecular size and shape of the lubricant, its interaction with the surface and its frictional response under nanoconfinement," explains Federici.



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The anion size determines the structure of an ionic liquid confined between two surfaces separated by a few nanometers.

The team simulated the behaviors of two ionic liquids containing the cation 1-butyl-3-methylimidazolium (BMIM). In one liquid, BMIM was paired with the comparably sized anion bis(trifluoromethanesulphonyl) amide (NTF2), whereas the other ionic liquid contained the much smaller anion tetrafluoroborate (BF4). Both simulations used neutral crystalline silica surfaces with protruding hydroxyl (OH) groups to confine the liquids.

"The two liquids responded to the same silica surface in very different ways," notes Federici. In particular, the anion size is critical in determining how the liquid molecules arranged themselves against the surfaces. As NTF2 is too large to fit between silica's OH groups, the ionic liquid containing BMIM and NTF2 forms neutral layers containing equal numbers of anions and cations. In contrast, the BMIM–BF4 liquid forms a layer of BF4 anions closer to the silica surface, followed by alternating layers of cations and anions (see image).

Interestingly, this layering affects the ability of the ionic liquids to flow between the surfaces. When the BMIM–NTF2 layers flow past each other, similarly charged ions in adjacent layers face each other, making the structure unstable and eventually forcing it to rearrange. The BMIM–BF4 liquid is more stable, however, as ions of the same charge are not brought so close together.

The simulations throw light on a puzzling experimental result, namely that BMIM–NTF2, which is less viscous than BMIM–BF4 under normal conditions, becomes more viscous than it when the liquids are confined between planes separated by a few nanometers.

A more realistic model of the silica surfaces could offer even greater insight. Currently, the team simulates crystalline silica with a similar density to that of glass. However, as glass is amorphous, "its disorder may be an important factor in the structuring of ionic liquids at the interface," explains Federici.

1. Federici Canova, F., Matsubara, H., Mizukami, M., Kurihara, K. & Shluger, A. L. Shear dynamics of nanoconfined ionic liquids. *Physical Chemistry Chemical Physics* **16,** 8247–8256 (2014).

Graphene

Finding catalytic success with three-dimensional nanopores

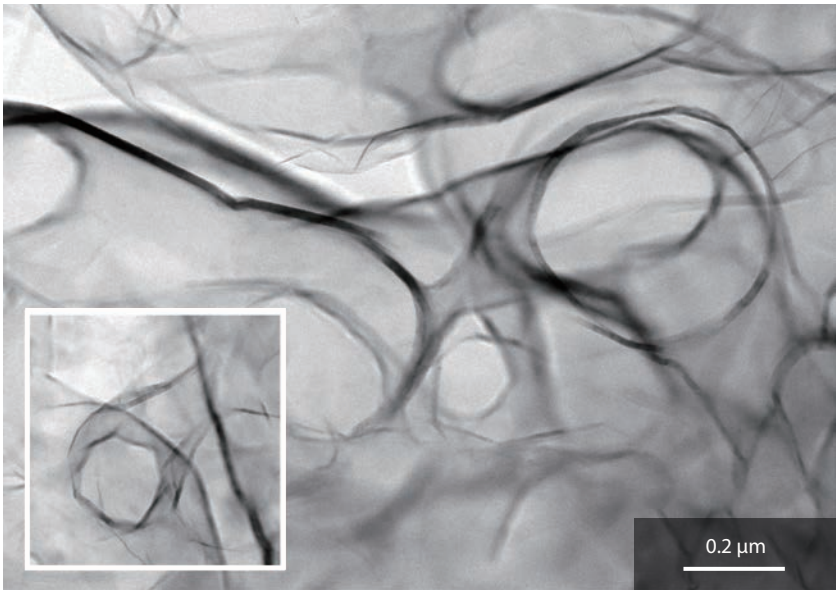
Atomic defects in a uniquely shaped material turn graphene into a metal-free catalyst for fuel cells and lithium–air batteries

AIMR researchers have discovered how to unleash the promising catalytic activity of graphene by tweaking its chemical structure and twisting it into a three-dimensional (3D) nanoporous framework.

Fuel cells and lithium–air batteries generally use expensive components, such as platinum-based electrodes, to transform oxygen into electricity. Researchers have been considering graphene — a single layer of carbon atoms with metal-like properties — as a cheaper alternative. However, progress in this area had been hindered by graphene's low chemical reactivity.

Now, Yoshikazu Ito, Mingwei Chen and colleagues from the AIMR at Tohoku University have developed an innovative way to turn flat graphene sheets into 3D objects using 'bicontinuous' nanoporous nickel templates[1]. These materials resemble a type of metallic sponge with flat surfaces infused with numerous nanoscale openings, known as nanopores. Chemical vapor deposition of benzene gas into the nickel nanopores, followed by acid treatment to remove the template, produced 3D graphene — a structure with an astonishingly high conductivity not far removed from that of its flat counterpart.

The team uncovered a connection between small pore size and high conductivity in 3D graphene and realized that the build-up of geometric defects needed to turn flat graphene into 3D nanopores was playing a role. Because these defect sites are electronically active, they conjectured that the sites could also serve as catalytic reaction sites.



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Tiny nanopores in a three-dimensional graphene structure can serve as catalytic reaction sites for green energy technologies.

But to engineer a specific catalytic response toward the 'oxygen reduction reaction' used to power fuel cells and lithium–air batteries, the researchers had to introduce foreign nitrogen dopant atoms into the graphene structure. To do so, they switched to pyridine gas — a benzene-like molecule with one nitrogen and five carbon atoms — and deposited it onto the bicontinuous nickel template.

Analytical measurements revealed that the new, nitrogen-doped graphene also formed an ordered 3D framework with distinct nanopores (see image). When the researchers tested this material by plunging it into an oxygen-saturated electrolyte solution, they found that it had superb catalytic behavior — particularly the samples with the tiniest possible pore sizes.

"Smaller pore structures require more geometric defects due to the high-curvature structures they impose," explains Ito. "They also contain the highest pyridine nitrogen atom concentrations, and these dopant atoms create different kinds of geometric defects. This significantly enhances the nanoporous nitrogen-doped graphene's catalytic activity."

The team is now investigating how to further unleash the catalytic power of 3D graphene nanostructures by directing its activity toward the hydrogen evolution reaction that also plays a key role in batteries and fuel cells.

1. Ito, Y., Qiu, H.-J., Fujita, T., Tanabe, Y., Tanigaki, K. & Chen, M. Bicontinuous nanoporous N-doped graphene for the oxygen reduction reaction. *Advanced Materials* **26,** 4145–4150 (2014).

Polymers

Nanoscale nudges reveal critical clues

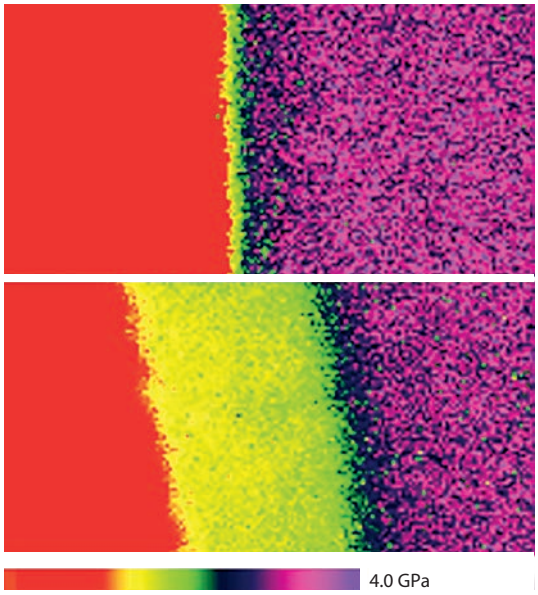
The forces holding multilayered polymer devices together can be mapped using high-resolution 'nanomechanical' probes

Small variations in mixing at polymer interfaces can have a large effect on how devices such as photovoltaic cells and membranes perform. Dong Wang from the AIMR at Tohoku University and colleagues have used an innovative technique known as quantitative nanomechanical mapping (QNM) to simultaneously acquire microstructural and mechanical information on polymer interfaces[1]. This information may make solving future adhesion problems significantly simpler.

One of the fundamental issues facing manufacturers of polymer-based devices is quantifying how different layers diffuse and entangle together after processing treatments. Many analytical techniques have been developed to study the interpenetration of long molecular chains into each other's domains. However, most of these methods provide only the concentration gradients of different components. The interfacial mechanical properties, which are tightly linked to a polymer's applications, are difficult to measure at small scales.

Wang and colleagues turned to the capabilities of atomic force microscopy (AFM) to detail the unique physics of polymer interfaces. Normally, researchers use resonant 'tapping' signals from an AFM probe to trace out detailed, three-dimensional profiles of scanned surfaces. These tapping signals can also gauge the mechanical forces between a polymer and the probe. But such AFM force modes have slow data acquisition rates and require nontrivial analytical techniques to convert the measured mechanical forces into material properties.

The newly developed QNM imaging mode for AFM dramatically speeds up and simplifies mechanical measurements by detecting the maximum force applied to a surface during a probe tap. Then, by using this 'peak force' signal as a damage-preventing feedback control loop, the tapping signals can scan rapidly across a sample and map out regions of different physical force with nanoscale precision.



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A new atomic force microscopy imaging technique that reveals how polymer interfaces (green region) broaden and diffuse over time provides information that may help extend the lifetimes of devices such as plastic solar cells.

The researchers examined interfaces formed between poly(vinyl chloride) and poly(n-butyl methacrylate), two plastics that are fully mixable, to test for diffusion-induced effects with QNM. The resulting nanomechanical maps revealed clear stiffness signatures of the polymer components and a distinct bulge at the interface (see image). By tracking how this zone broadened and mechanically deformed over time, the team acquired a wealth of new physical and chemical data: the interface's diffusion kinetics, microstructures and glass transition temperatures were identified with a ten-nanometer resolution.

"What is most striking about this method is its ability to assess small differences in the mechanical properties of materials over very short length scales using high-resolution AFM," says Wang. "This has not been possible previously and provides a new route to investigate the bonding between polymer multilayers."

1. Wang, D., Liang, X., Russell, T. P. & Nakajima, K. Visualization and quantification of the chemical and physical properties at a diffusion-induced interface using AFM nanomechanical mapping. *Macromolecules* **47,** 3761–3765 (2014).

Biosensors

A gentler route to hydrocarbon electrodes

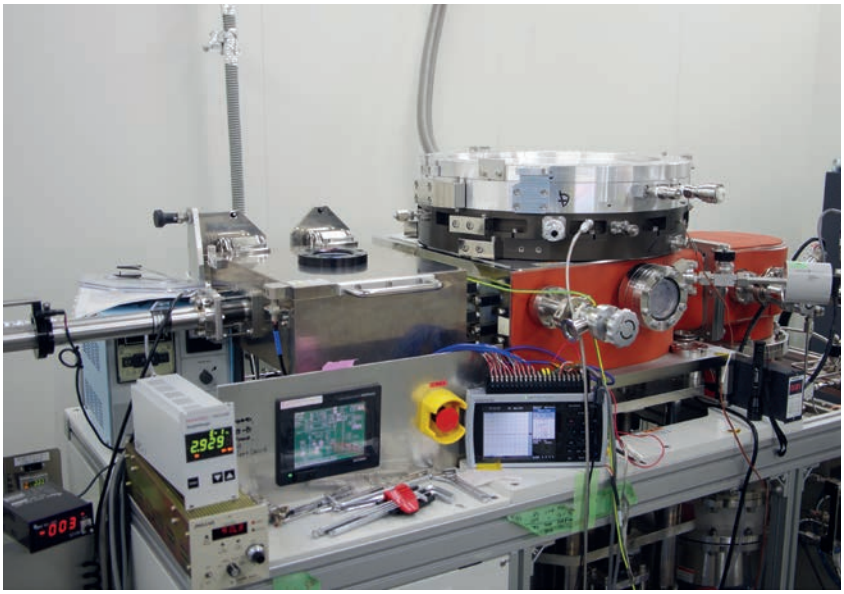
A new deposition technique has been used to form conducting films for detecting biological molecules

A new technique for creating amorphous hydrocarbon films that employs much milder conditions than conventional methods has been applied by Yoshiyuki Kikuchi and colleagues of Seiji Samukawa's and Tomokazu Matsue's laboratories at the AIMR, Tohoku University to fabricate electrodes for electrochemical sensors[1].

Amorphous hydrocarbon films are promising for use as components in biomedical sensors, as they are biocompatible, chemically stable and conduct electricity well. These properties make them suitable as electrode coatings in such sensors. But conventional techniques for creating amorphous hydrocarbon films require high temperatures and plasma — a gaseous soup of charged particles — both of which can damage the semiconductor substrates beneath the films.

The new technique uses two reaction chambers separated by a perforated barrier (see image). Argon gas is injected into the upper chamber, where microwaves excite it to form a plasma containing positive argon ions. Meanwhile, the carbon-based compound toluene is injected into the lower chamber, from where it leaks into the upper chamber through the holes in the barrier.

The positive argon ions partially break up the toluene molecules, which then return to the lower chamber and adsorb on a silicon substrate at a temperature of –50 degrees Celsius. Argon ions follow the same path, but pick up an electron as they pass through the perforated barrier, creating a stream of neutral argon atoms; this neutralization technology of argon was developed by Samukawa's group in 2000. These atoms hit the carbon-based fragments stuck to the silicon, helping to knit the molecules together into a continuous film. Crucially, the perforated barrier blocks any ultraviolet light emitted by the plasma, which would otherwise damage the precursor molecules and substrate.



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A new deposition technique allows amorphous hydrocarbon films to be fabricated under much milder conditions than conventional methods.

The researchers found that the film was composed of an interconnected network of molecules called polyaromatic hydrocarbons and could conduct electricity reasonably well. Tests showed that the film had a low electrical resistance and fast electron transfer, ideal properties for an electrochemical sensor.

The team improved the technique by producing just the right balance of pressures between the two chambers, to enable ideal mixing of argon and toluene. They also boosted the film's conductivity by adding nitrogen gas to the argon stream — this probably resulted in nitrogen atoms being incorporated into the finished film, a process called nitrogen doping that helps make the material's electrons more mobile. "Nitrogen doping improves the electrode performance," explains Kikuchi.

The researchers are currently collaborating with another group to develop an amorphous hydrocarbon electrode for a sensor that could be used for a range of bioimaging applications, such as tracking the release of neurotransmitters from neurons.

1. Kikuchi, Y., Wada, A., Kurotori, T., Nakano, M., Inoue, K. Y., Matsue, T., Nozawa, T. & Samukawa, S. Conductive amorphous hydrocarbon film for bio-sensor formed by low temperature neutral beam enhanced chemical vapor deposition. *Carbon* **67,** 635–642 (2014).

Graphene

Customized from the bottom up

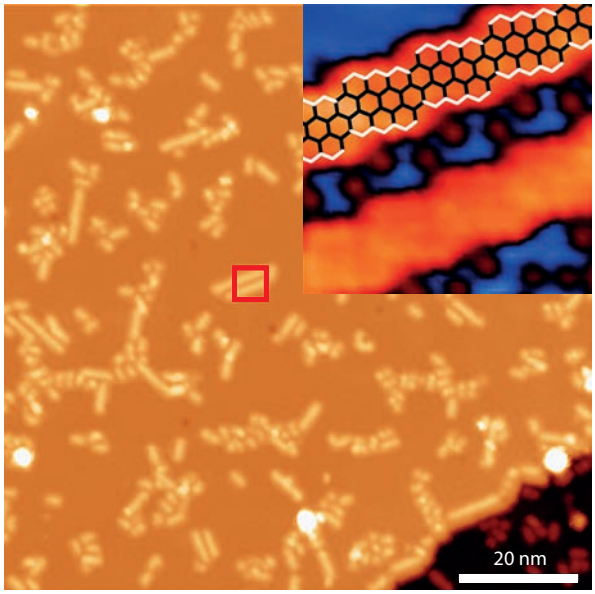
A surface-assisted chemical reaction gives unprecedented control over graphene 'nanoribbons' for future nanodevices

An interdisciplinary team has devised a way to self-assemble defect-free graphene nanostructures right where they are needed by exploiting the reaction-directing properties of copper surfaces[1]. This is a significant advance since high-speed graphene transistors can outpace current silicon technology, but fabricating these atom-thin sheets of carbon into device structures had been problematic.

The team, which is led by Patrick Han and Taro Hitosugi from the AIMR at Tohoku University, is investigating experimental materials known as graphene nanoribbons (GNRs) for use in tiny transistor devices. The electronic states of these narrow graphene strips strongly depend on the atoms bordering their edges. A GNR is semiconducting when the edge carbons bond into an 'armchair' configuration, whereas a 'zigzag' configuration of edge carbons produces a metallic GNR with quantum confined spin states.

Because conventional circuit lithography inevitably introduces defects into GNRs, recent studies have explored a more direct, 'bottom-up' approach — growing graphene strips atom by atom by depositing molecular precursors onto metal surfaces. Typical strategies use chemically active precursors with relatively inert gold and silver substrates to give molecules many chances to interact with one another. But these methods have so far produced only armchair GNRs.

To synthesize zigzag nanoribbons, the researchers investigated whether a more reactive copper surface could direct a molecular polymerization reaction. "On surfaces like copper, molecules are less free to diffuse randomly and are more inclined to interact with an ordered lattice of metal atoms," explains Han.



© 2014 Patrick Han

Scanning tunneling microscopy image of self-assembled graphene nanoribbons on a copper surface. The 'zigzag' ribbon structures are highlighted by white lines in the high-resolution inset.

The researchers deposited precursors known as 10,10'-dibromo-9,9'-bianthryl monomers onto a copper surface and then used atom-resolved scanning tunneling microscopy to scrutinize the structures of samples produced at different annealing temperatures. They discovered that at room temperature the precursors self-assembled into narrow chains that preferentially grew in only six directions along the copper lattice. Stepwise heating to 500 degrees Celsius caused these chains to bunch into islands before joining up into periodic regions of zigzag nanoribbons (see image).

Further experiments revealed that the bromine atoms on the precursor helped hold the molecules into the zigzag arrangement at high temperatures until the graphene polymerization reaction occurred at 500 degrees Celsius. This is surprising since copper surfaces normally break off bromine atoms from aromatic molecules at room temperature.

The scientists anticipate that the fine control over nanoribbon length, direction and edge conformation this technique offers will spur more studies into surface-directed chemistry. "By exploiting the properties of a reactive surface, we can determine which nanoribbon structure will form and restrict its growth to specific directions," says Han.

1. Han, P., Akagi, K., Canova, F. F., Mutoh, H., Shiraki, S., Iwaya, K., Weiss, P. S., Asao, N. & Hitosugi, T. Bottom-up graphene-nanoribbon fabrication reveals chiral edges and enantioselectivity. *ACS Nano* **8**, 9181–9187 (2014).

Electrochemistry

Mapping a battery electrode

Microscopy technique tracks the flow of lithium ions in a common cathode material

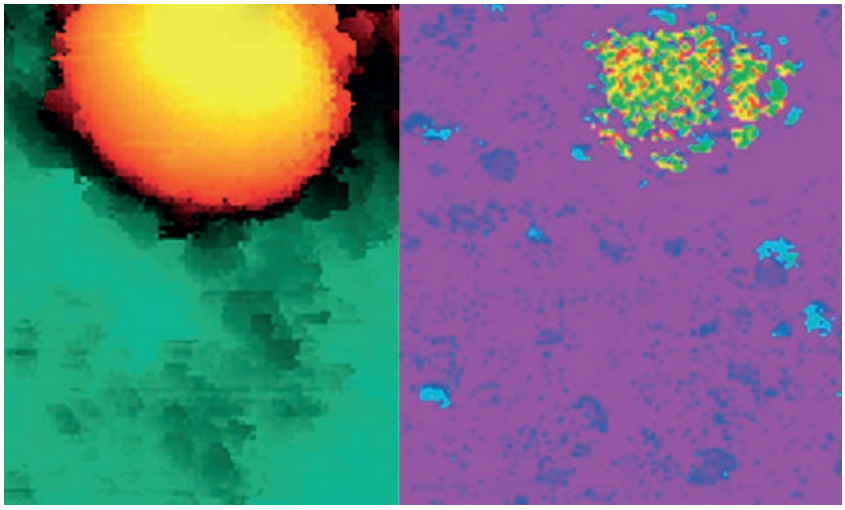
A powerful new imaging technique has mapped the reactivities related to lithium-ion transport in an electrode for the first time, which will lead to battery designs with higher performances.

Lithium-ion batteries are widely used to power mobile devices, but some aspects of their operation are still veiled. Studying the interaction between lithium ions and electrodes has been particularly challenging due to a lack of suitable analytical techniques for measuring reactivities.

Now, Tomokazu Matsue, Yasufumi Takahashi and Akichika Kumatani of the AIMR at Tohoku University and colleagues have developed a nano-scanning electrochemical cell microscope that can record the electrochemical properties of a lithium iron phosphate ($LiFePO_4$) electrode[1]. "This is the first time anyone has visualized the reactivity of an electrode surface," says Takahashi.

The microscope uses a pipette probe whose aperture diameter is roughly 50 nanometers. The probe contains a solution of lithium ions and scans slowly across the electrode surface. Whenever the solution within the nanopipette touches the electrode, lithium ions flow between the two, creating an electrical current. This allowed the researchers to map an electrode's landscape to a scale of about 100 nanometers and to investigate its electrical properties at specific points.

The team tested their device on a typical electrode containing a blend of $LiFePO_4$ and acetylene black. While being cheap and environmentally benign, $LiFePO_4$ suffers from a low electrical conductivity. Acetylene black improves the electrode's conductivity, but it reduces the battery's overall energy capacity since it cannot store lithium ions.



Modified, with permission, from Ref. 1 © Y. Takahashi et al.

Scanning electrochemical cell microscopy is used to map the topography of a lithium iron phosphate particle in a battery electrode (left), as well as measure the current that flows into it (right; red corresponds to the maximum current of 143 picoamperes).

The nano-scanning electrochemical cell microscope confirmed that lithium ions flowed readily into micrometer-sized $LiFePO_4$ particles that were embedded in the electrode, but did not enter regions made of acetylene black. The probe was sensitive enough to target individual particles, without interference from neighboring materials (see image).

By altering the concentration of lithium ions in the electrode, the nanopipette probe could also reveal how charging or discharging affected the voltage at specific points of the electrode. Stringing together snapshots of the process taken every 10 milliseconds produced a movie of an individual $LiFePO_4$ particle's electrochemical behavior.

The researchers also analyzed individual nanoparticles of $LiFePO_4$ on a platinum plate to discover how the crystal structure and particle orientation affected the way lithium ions flowed through it. They are now carrying out further experiments on these properties, which might help to optimize the position and structure of $LiFePO_4$ particles in electrodes to boost battery performance.

1. Takahashi, Y., Kumatani, A., Munakata, H., Inomata, H., Ito, K., Ino, K., Shiku, H., Unwin, P. R., Korchev, Y. E., Kanamura, K. & Matsue, T. Nanoscale visualization of redox activity at lithium-ion battery cathodes. *Nature Communications* **5**, 5450 (2014).

Microscopy

Ultrasharp probing of solar cells

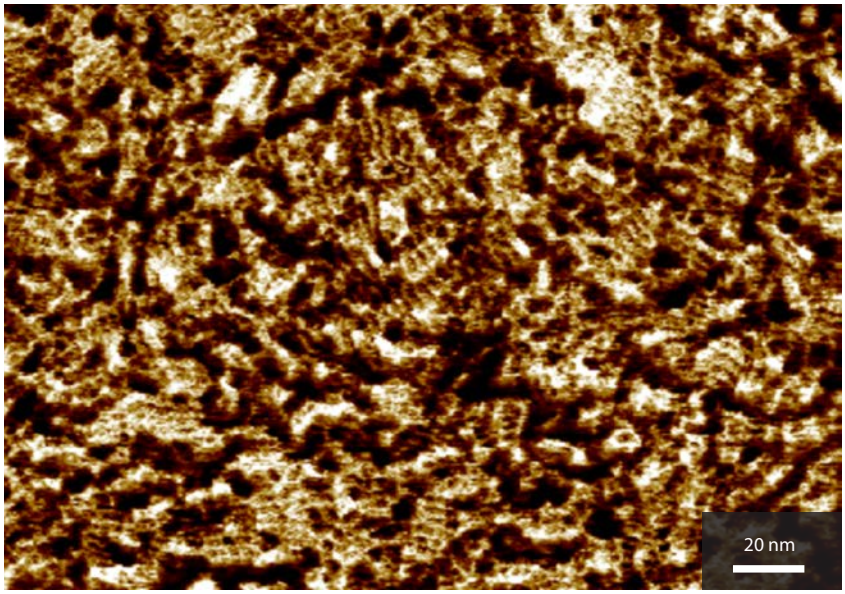
High-resolution atomic force microscopy reveals the inner workings of low-cost photovoltaic devices

An international team has captured unprecedented, three-dimensional (3D) images that reveal how polymers are organized in 'bulk heterojunction' (BHJ) organic solar cells[1] — one of the most promising green devices for generating renewable electricity in an economically viable way. These new images can help settle long-standing debates on how molecules assemble at electrode interfaces, leading to improved manufacturing strategies.

The light-harvesting components of BHJ organic solar cells contain two materials that possess opposing electron-accepting and -donating abilities. To ensure efficient collection of solar energy, these materials must be blended until they are separated by no more than a few tens of nanometers. Most analytical techniques, however, can observe blended regions only in flat, two-dimensional planes, whereas actual devices are 3D.

Now, Dong Wang, Ken Nakajima and Thomas Russell from the AIMR at Tohoku University have used atomic force microscopy (AFM) to explore morphologies inside BHJ devices. AFM employs tiny needle-like probes to trace the topology of 3D surfaces, but it normally has trouble resolving polymer structures at molecular levels. The team overcame this limitation by using ultrasharp AFM tips that, as they are only a single nanometer wide, can image incredibly fine details on surfaces.

The researchers first prepared a standard BHJ device containing an aromatic electron-donor polymer known as PTB7 and a 'buckyball'-like electron-acceptor material called PCBM. They then exposed the kinetically active working layers inside the BHJ by using high-energy argon ions to etch away the outer layers of the polymer blend.



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An atomic force microscopy phase image showing the arrangement of polymer crystals inside solar cells with a nanometer-scale resolution.

Subsequent AFM, X-ray scattering and electron microscopy measurements revealed that the device's active layer contained a continuous network of PTB7 fibrils, separated by tens of nanometers, interpenetrated by pathways of PCBM strands. This morphology changed at the electrode-contacting outer surface, where PTB7 crystals formed with PCBM aggregates embedded in-between (see image).

The researchers prepared devices containing different proportions of PTB7 and PCBM and discovered that the solar conversion efficiencies of these devices corresponded neatly to the length scales of the morphologies observed by AFM. According to Wang, this is clear evidence that three main factors — the PTB7 fibrils, the PCBM network, and the active mixing region — must be optimized to produce high-performance organic solar cells.

"These morphologies suggest that next-generation polymers need fibrils with fewer defects and better connectivity," says Wang. "For the acceptor side, new materials that can form better and finer network domains will prove critical."

1. Wang, D., Liu, F., Yagihashi, N., Nakaya, M., Ferdous, S., Liang, X., Muramatsu, A., Nakajima, K. & Russell, T. P. New insights into morphology of high performance BHJ photovoltaics revealed by high resolution AFM. *Nano Letters* **14,** 5727–5732 (2014).

IN THE SPOTLIGHT

The AIMR has grown rapidly since its inauguration in 2007, now with over 150 leading researchers from all over the world, including 30 internationally renowned principal investigators who are charged with pioneering new and innovative breakthroughs in materials science. The institute is also active in developing young, promising researchers with a focus on strong cross-disciplinary collaboration and creativity. AIM*Research* spotlights these talented researchers of the present and future, detailing their daily research activities and scientific ambitions.

INTERNATIONAL SYMPOSIUM

Published online on 31 March 2014

Materials–maths fusion research enthuses symposium attendees

The AIMR International Symposium (AMIS) 2014, held in Sendai on 17–19 February, showcased how the institute's unique brand of mathematics–materials fusion research is already making positive contributions to society

The main objective of AMIS 2014 was to share discoveries from the AIMR's recent institute-wide infusion of mathematics into materials science research while learning from other innovators in the field. Leading experts in materials science from Japan and overseas attended the gathering to explore the theme "Toward emergence of new materials science with mathematics collaboration." Preserving the strong international interest of the previous year, the 236 participating researchers represented 52 organizations and 13 countries.

Susumu Satomi, president of Tohoku University, welcomed the participants. In his address, he emphasized the crucial role of the AIMR in upholding Tohoku University's commitment to research by "creating a new paradigm of 'mathematics-driven materials science'." Satomi added: "In particular, materials science can contribute enormously to society, creating a basis for green materials and cultivating the potential of natural energy resources to resolve environmental problems." Essential to achieving this goal, he noted, was the AIMR's extensive global network, with 22 overseas partner institutions, including its AIMR Joint Research Centers at the University of Cambridge, UK; the University of California, Santa Barbara (UCSB) in the US; and the Institute of Chemistry, Chinese Academy of Sciences, China.

Speaking next, Akira Ukawa, deputy program director of the World Premier International Research Center Initiative (WPI), further underscored the importance of fundamental and innovative science for societal development. Ukawa highlighted the many ideas that have emerged from the reciprocal influence between mathematics and experimental science, such as the theory of relativity and quantum mechanics. "Mathematics and the sciences are most fruitful when they work together and collaborate together," he said. "So be ambitious. History is on your side."

Almost 240 researchers from over 50 organizations and 13 countries attended the AIMR International Symposium in Sendai in February 2014 to share knowledge under the banner of "Toward emergence of new materials science with mathematics collaboration."

In her welcoming address, AIMR Director Motoko Kotani shared the story of the AIMR's transition toward a collaborative materials and mathematics research culture, which she initiated in 2011. "It took us two years to reorganize our internal structures," she said. One of the critical moves was the establishment of three Target Projects, which use mathematics to clarify principles and mechanisms behind physical systems, and that were carefully selected for their potential to flourish in the new context of fusion research. These reforms have already enabled fluent interdisciplinary exchange, said Kotani, a trained mathematician herself. "We are very happy that, with this symposium, we can share some of our emerging results."

Powerful prose

The day's program proceeded with a series of invited speakers. Hirosi Ooguri of the California Institute of Technology, US, and the Kavli Institute for the Physics and Mathematics of the Universe, the University of Tokyo, drew on his decades of work at the interface of mathematics and theoretical physics to share some unexpected

connections. "Mathematicians look for things that are universal. Physicists want immediate results," said Ooguri. Given the differences in the terminology, motivation and work habits of mathematicians and physicists, he stressed the importance of translating a problem from one 'language' to the other to improve the potential to find a solution.

Chemist Håkan Wennerström from Lund University in Sweden began by detailing findings on the non-equilibrium formation processes of mesoporous particles — materials that contain pores of 2–50 nanometers in diameter. Moving on to describe the presence of non-equilibrium systems at air–water interfaces where water evaporates, such as the surface of the skin or eye, Wennerström noted that understanding this phenomenon could translate into the improved delivery of drugs.

Speaking next was Steven Louie, a condensed matter physicist from the University of California, Berkeley in the US. Louie focused on his recent work on graphene, a material composed of an atom-thick sheet of carbon. Graphene is remarkably strong, light and transparent, and conducts heat and electricity with negligible resistance. Louie moved on to discuss findings on the optoelectronic properties of graphene, which will enable exciting new generations of electronic devices.

Presentations by the final two opening speakers demonstrated the powerful ability of mathematics to fuel discoveries in materials science. Physicist Qi-Kun Xue, vice-president of Tsinghua University in China and a principal investigator at the AIMR, related his experimental confirmation of the quantum anomalous Hall effect in magnetic topological insulators — something that had previously been only a theoretical conjecture. "This observation completes all the three quantum Hall effects," noted Xue.

James Langer, a theoretical physicist from the UCSB, wrapped up the opening session by offering insight into the dynamics of glass using a mathematical model. "The glass bubble is the most incredibly beautiful, important and deep mystery that faces us in classical physics these days," said Langer. To address this challenge, "we have to focus on really simple and realistic models of glass-forming materials."

Small energy: Big impact

AMIS 2014 spanned 3 days and featured 6 plenary sessions, 4 parallel lecture tracks and a poster session. A total of 32 scientists from 6 countries spoke about subjects ranging from non-equilibrium systems and mathematics to soft materials and energy materials, while almost 100 posters revealed the latest findings from researchers at the AIMR.

James Langer, theoretical physicist from the University of California, Santa Barbara in the United States offered new insight into the dynamics of glass using a mathematical model.

Akira Ukawa, deputy program director of the World Premier International Research Center Initiative (WPI), delivered a historical take on the potential rewards of merging materials science research with mathematics.

Masaru Tsukada, administrative director of the AIMR, brought the events to a close. In his presentation, he introduced a fourth Target Project — Core Technology for Nano Energy Devices — newly created to ensure the transfer of materials science research for the benefit of society. The project will develop systems for renewable energy applications and innovative processing technologies for sustainable, green materials. In his valediction, Tsukada extended an invitation to all participants to return to Sendai for next year's symposium, AMIS 2015, scheduled to be held on 17–19 February.

The symposium marks the end of another busy year for the AIMR. "When we first embarked on our reorientation, the WPI's progress report said that while our proposal was attractive, they were concerned about whether our plan could be realized," reflected Kotani, speaking after the event. "This year, the report notes that the AIMR has progressed much faster than expected." Among its many achievements in 2013, the institute published particularly novel research on bulk metallic glasses in *Science*. Kotani predicts that the AIMR's new direction will result in further breakthroughs in understanding of the structure and properties of a host of materials, including graphene, carbon networks and nanoporous gold. "We took the right direction," asserted Kotani. "This is one of our strong beliefs." ■

DIRECTOR'S INTERVIEW

Published online on 26 May 2014

Exporting mathematics–materials collaboration research to the world

Under Director Motoko Kotani's leadership, the AIMR has made mathematics–materials research a global priority

Two years ago, the AIMR welcomed mathematician Motoko Kotani as its new director. Since then, the institute has established itself globally through its innovative focus on mathematics-flavored materials science research. AIM*Research* spoke to Kotani about her successes in extending the AIMR's overseas reach through strong research partnerships and creating an international work culture.

AIM*Research*: *The AIMR continues to develop its international network through joint research centers, partner institutions and inter-faculty exchange agreements. What have these various forms of cooperation achieved?*

After taking on the directorship, I introduced a program of joint research centers where postdoctoral researchers can conduct collaborative research. Of the 15 international institutes with which the AIMR has already established agreements, we have built closer relationships through three of the joint research centers in particular: the University of Cambridge in the UK, the University of California, Santa Barbara (UCSB) in the US, and the Institute of Chemistry, Chinese Academy of Sciences. These centers have significantly contributed to our global visibility through the publication of research and co-organizing workshops that bring recognition to the researchers involved as much as the institutes they represent.

Motoko Kotani, director of the AIMR.

AIM*Research*: *What plans do you have to extend such partnerships in the coming years?*

In 2014, we will organize a workshop with the Australian National University and a Tohoku Forum at the University of Cambridge, which will integrate research from the AIMR and our host institute, Tohoku University.

Since we are not a very large institute, our emphasis is on enhancing — as opposed to expanding — our global network. One way that we strengthen the depth of our collaborations is by setting common research agendas with our partners that create a bridge for the two-way exchange of information and researchers.

We are establishing a new joint research center at the University of Chicago in the US and are in discussion with the Chinese Academy of Sciences to create another laboratory in Beijing, together with Tsinghua University. We would also like to extend our relationship with Fraunhofer-Gesellschaft beyond current agreements with three of the organization's institutes. I would like the AIMR to move toward more joint research through shared grants that can be divided between two countries, for example.

During her tenure as director of the AIMR, Kotani has set a new direction for the AIMR through mathematics-driven materials research.

AIM*Research*: *The AIMR is recognized for cultivating a fertile environment for the free exchange of ideas and every year attracts more of the brightest minds from all over the globe. How have you managed to create such an open and inclusive research atmosphere?*

Creating a favorable environment for research is crucial to science. Many researchers are interested in coming to Japan because of its reputation for high-quality research but are deterred by the language barrier. Here at the AIMR, the working language is English. The highly motivated staff at our administrative office help foreign researchers to transition to and settle in Japan, and provide them with essential information and support services for maneuvering the grant application system. In addition, we have initiated a scheme of jointly appointing academics with external partner universities, which affords researchers increasing flexibility and mobility.

Furthermore, I offer many incentives to active researchers. Here at the AIMR, successful researchers receive merit-based benefits like more research space or a salary increase. This attracts very ambitious individuals — the kind of researchers I want at the AIMR.

AIM*Research*: *According to the latest WPI program review, the AIMR has made "remarkable progress" since introducing a new mathematics–materials approach to research in 2012. How were you able to achieve so much so quickly?*

Since the establishment of the AIMR, our researchers have been making commendable progress in taking their research to the next level. Creating a new vision for the AIMR through our mathematics–materials approach allowed us to amalgamate their collective achievements and to direct our resources and research power toward a common goal, thereby multiplying the strengths of the institute. Materials science is a very complex and wide-ranging research area, which makes it impossible to be recognized worldwide across all areas of the field. Therefore, we decided to focus on a few target projects that fit within the mathematics–materials framework. We have identified problems to be studied that are challenging — but also very attractive — from the viewpoints of both mathematics and materials science.

AIM*Research*: *2014 marks the eighth year of a ten-year funding commitment to the AIMR from the WPI program. What plans do you have to ensure the long-term future of the institute?*

I have met several times with Susumu Satomi, president of Tohoku University, to highlight the AIMR's contributions to Tohoku University. Despite the AIMR's small number of principal investigators, half of whom are from abroad, we bring in 5–6 per cent of the external research funds generated by the university. I think that this is remarkable.

Convinced by the AIMR's significant contribution to system reforms at Tohoku University, the president formally committed the university to establishing a new permanent framework that focuses on globalized, interdisciplinary research across several areas, including mathematics and materials science. The organization will be established in a few months.

The long-term sustainability of the AIMR is very important, especially for young researchers who have only just set out in our new direction. They are doing very good work and it is my responsibility to help them to continue with their research — and what better place than here at the AIMR? ■

INTERNATIONAL SYMPOSIUM

Published online on 28 July 2014

World-leading WPI initiative showcases materials science innovation at E-MRS Spring Meeting

An attentive audience met researchers from the AIMR at the annual Spring Meeting of the European Materials Research Society in France

From a new spin on electronics to tiny biological superhighways and beaming carbon-based transistors, researchers from the Advanced Institute for Materials Research (AIMR) presented their vision of the future of materials science at the 2014 Spring Meeting of the European Materials Research Society (E-MRS), the 32nd in a series of annual meetings held since 1983. "The E-MRS Spring Meeting is one of the most important conferences on materials science for the global community," notes Masaru Tsukada, administrative director at the AIMR.

This year's meeting, held on 26–30 May 2014 in Lille, northern France, was the society's largest gathering since its establishment in 1983. Among the estimated 3,100 participants was a 44-strong team from Japan representing the World Premier International Research Center Initiative (WPI), a funding body that supports centers of excellence in basic science.

The four WPI participating institutes — the AIMR, the International Center for Materials Nanoarchitectonics, the Institute for Integrated Cell-Material Sciences and the International Institute for Carbon-Neutral Energy Research — shared their latest research with an attentive international audience at the meeting. Fourteen researchers from the AIMR — the highest number among the WPI institutes — gave presentations in subjects that included spin transport, protein vehicles and organic superconductors.

The highlight of the WPI team's schedule was a half-day symposium titled "Japan in Motion." Through a series of talks, the scientists introduced new ideas that are seizing the materials science community, from an atomic and molecular control approach to designing new structures based on nanoscale building blocks, to the successful alliances between materials science and mathematics that have emerged from a directed shift toward fusion research.

Eiji Saitoh shared his expertise in spintronics technology at the 2014 E-MRS Spring Meeting in France.

"Japan in Motion was a huge success," says AIMR director, Motoko Kotani, who at the meeting was approached by many researchers eager to collaborate with the AIMR or move to Japan to conduct research at the institute. The symposium itself attracted an impressive 70 participants, and 400 individuals visited the associated WPI booth, including the current E-MRS president, Thomas Lippert, and former president, Ian Boyd.

Conducting spin

In addition to the Japan in Motion event, WPI researchers shared their research at sessions organized over the course of the five-day meeting. In his presentation, Eiji Saitoh, a principal investigator at the AIMR, introduced his recent contributions to the technology of spintronics.

Spintronics seeks to manipulate the properties of spin and charge inherent in electrons for microelectronic device production. The technology is used in all commercially available disk drives today, and increasing control over electron spin could lead to even speedier data transfer

and denser storage capacities. "The AIMR is one of the strongest institutes in the world for spintronics research," says Saitoh.

Saitoh's research builds on observations made in the early eighteenth century by German physicist Thomas Johann Seebeck, who discovered that temperature differences in a conductor can generate an electric current — a phenomenon aptly named the Seebeck effect. In 2008, Saitoh led the team of researchers that observed an analogous effect in electron spins in a magnet, identified as the spin-Seebeck effect. He has since been able to generate and measure a spin 'voltage' resulting from a change in temperature in a metal or insulating ferromagnet, an effect that could be exploited in spintronic devices or to improve the efficiency of existing heat sensors and waste heat recycling systems.

Intrigued by Saitoh's presentation, a researcher from Germany suggested a method that could be used to control molecular spin. In a separate session, an independent investigator at the AIMR, Shigemi Mizukami, also shared his success in growing new manganese-based materials that could lead to terahertz-scale spintronic devices.

Researchers from around the world visited the WPI booth to find out how they could collaborate with interdisciplinary research centers in Japan like the AIMR.

Protein porters

Improving energy efficiency by drawing inspiration from nature was central to the work presented by Aurélien Sikora, a research associate at the AIMR.

One natural system that ranks especially high on the energy-efficiency ladder is the motor protein kinesin — the subject of Sikora's research. "Nature has a lot to teach us," says Sikora. "The efficiency of motor proteins in energy conversion is unbeatable. We have to understand how to achieve such a level of performance to reduce energy waste and pollution."

When loaded with goods, kinesin walks along microtubule roadways to transport its cargo throughout the cell. By turning kinesin proteins on their backs, scientists have been able to send microtubules 'crowd surfing' on the collective movement of the upward-facing kinesin legs. Sikora and his colleagues were able to demonstrate for the first time the potential for improving control of microtubule movement by confining the kinesin motors to narrow tracks made of carbon nanotubes.

Looking ahead, Sikora believes that using carbon nanotubes for protein-based transport could one day make it easier to control nanoparticle movement in biomedical devices, for example in conjunction with an electric field. Many participants at the E-MRS meeting were particularly interested in this ability to align the carbon nanotubes and asked numerous technical questions about Sikora's findings.

Organic benefits

A host of other fascinating materials were presented by AIMR researchers at the E-MRS meeting. Among them, principal investigator Mingwei Chen discussed the many merits of nanoporous metals fabricated through a process called dealloying, which gives them mechanical rigidity, a large surface area, electrical conductivity and high resistance to corrosion. And Taro Hitosugi, an associate professor, shared his findings from atomic-level investigations of a class of materials known as transitional metal oxides that exhibit compelling electron transport and magnetic properties.

In his poster presentation, Thangavel Kanagasekaran, a research associate at the AIMR, revealed he had successfully demonstrated an organic field-effect transistor that emits bright light at room temperature. Combining the ability to generate light with the electrical switching functionality of a transistor, this new class of optoelectronic device could improve visual display technologies and optical communication systems, and ultimately lead to the realization of electrically pumped organic lasers, he reported.

Kanagasekaran and the other AIMR and WPI delegates found that the interdisciplinary gathering in France offered an ideal venue to share ideas with their international counterparts. "All of the invited speakers from the AIMR took part in active and fruitful discussions with their peers," adds Director Kotani. "Our engagement with this interdisciplinary community has been very meaningful, and we will continue to pay attention to its activities." ■

INTERNATIONAL PARTNERSHIPS

Published online on 29 September 2014

Material benefits from US connections

The AIMR crosses the Pacific to strengthen its research ties with institutes in the United States

Two years ago, AIMR Director Motoko Kotani initiated the consolidation of the institute's many international alliances into focused centers for collaborative, multidisciplinary and high-impact research. This year, that effort continues with the introduction of an exciting new venture in the United States.

On 16 April, the AIMR signed an agreement to establish a joint research center with the University of Chicago, expanding on its three existing partnerships with the University of Cambridge, the Institute of Chemistry at the Chinese Academy of Sciences and the University of California, Santa Barbara (UCSB).

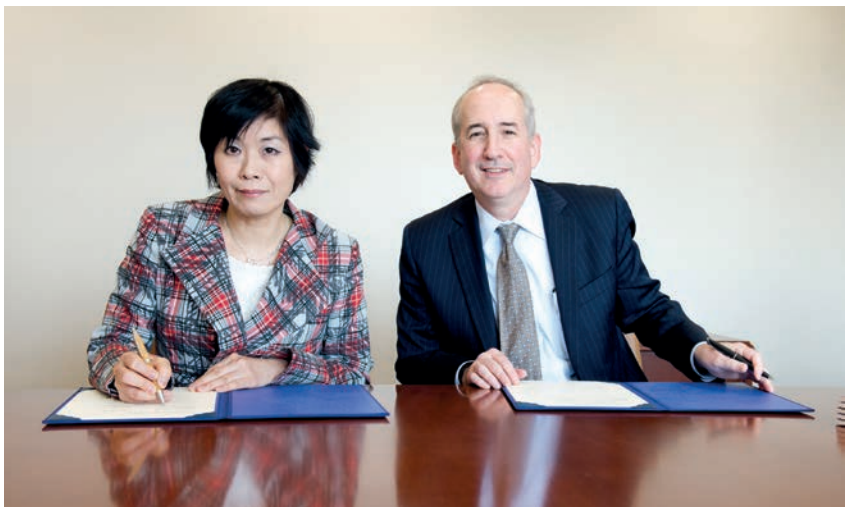
As well as enabling the two-way transmission and generation of knowledge through joint laboratories, workshops and researcher exchanges, this new connection further reinforces the strong relationship between two leading researchers in the field of spintronics — Hideo Ohno and David Awschalom. Ohno, a principal investigator at the AIMR, was the first to discover ferromagnetism in a superconductor, and he later developed an electrical 'switch' for turning a permanent magnet on and off. And Awschalom, a principal investigator at the University of Chicago's Institute for Molecular Engineering (IME), experimentally observed a phenomenon known as the spin Hall effect, which had been theoretically predicted over 30 years earlier. These and many other electron-spin-related discoveries in the last decades can enable faster information processing and data storage in spintronic devices.

Radical approach

The new Chicago relationship adds to an existing international partnership in the United States with UCSB. Researchers at the AIMR–UCSB joint research center are making unexpected connections in organic electronics, which may spawn an entirely new area of research.

As most organic radicals are highly unstable, researchers have tended to avoid investigating their potential for organic electronics. But Fred Wudl, chemistry and materials professor at UCSB and adjunct professor at the AIMR, wondered whether these radicals could be used in electronic devices. He posed the challenge of exploring this idea to AIMR–UCSB joint scientist Yonghao Zheng, who is currently based at Wudl's lab in Santa Barbara. The exercise proved worthwhile — Zheng discovered that the electronic properties of a stable organic radical can be simply altered by changing its temperature.

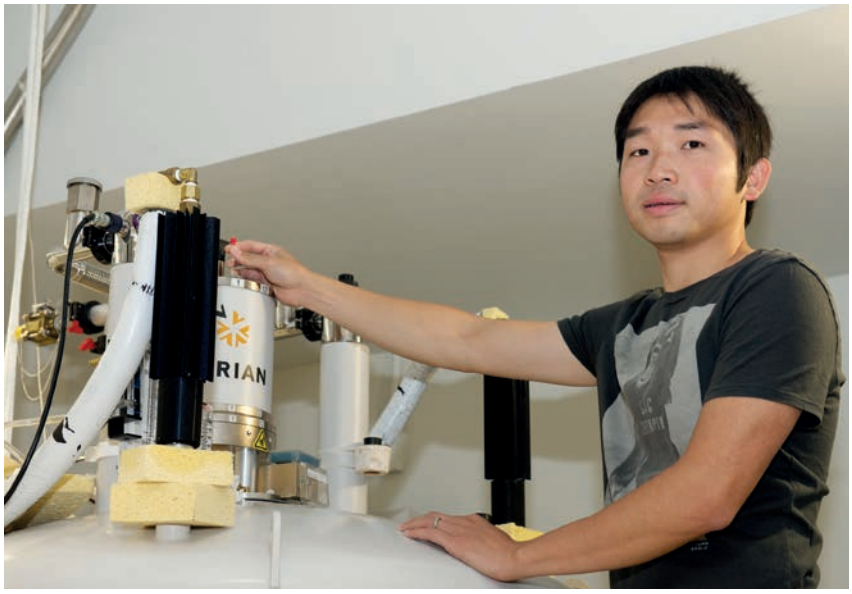
"This is a really exciting finding and could open up a new area of research for organic electronics," says Zheng. Organic materials are particularly attractive for use in electronics because their properties can be fine-tuned much more easily than inorganic materials, and they can be mass produced using simple, low-cost methods. Eventually, these materials could bring us flexible television screens and transparent photovoltaic wallpaper. "Organic electronics have the potential to make our lives more beautiful," says Zheng.



AIMR Director Motoko Kotani (left) and Eric Isaacs, provost of the University of Chicago, signed a joint agreement on 16 April 2014 to establish a joint research center.

Connecting researchers

In addition to studying the electronic properties of organic radicals, Zheng plans to investigate their magnetic properties by collaborating with a principal investigator at the AIMR, Katsumi Tanigaki, an expert on magnetism. Zheng also hopes to engage with the mathematicians at the AIMR to gain a better understanding of the reasons



AIMR–UCSB joint scientist Yonghao Zheng has discovered that the electronic properties of a stable organic radical can be simply altered by changing its temperature.

behind the phenomena he observes experimentally. A similar partnership has already been established at the AIMR between Hiroyuki Isobe, a principal investigator in the area of organic synthesis, and Director Kotani, who is a mathematician. Recently, this pair used geometry to describe and measure the length of finite-sized carbon nanotube molecules. "The AIMR is like one big family," says Zheng.

David Awschalom, a pioneer in the field of spintronics at the University of Chicago, presented his recent work at the first joint research center workshop organized between the University of Chicago and the AIMR.

"Everyone works very closely together, which really speeds up research."

Besides inspiring groundbreaking research, the collaboration between UCSB and the AIMR has benefited early career researchers like Zheng in many ways. "As a joint scientist, I have access to fabulous equipment at the UCSB Materials Department and can exchange ideas with top-level professors." The experience has expanded his research network and broadened his perspective. Crucial to that process have been the regular meetings and workshops between the two institutes, particularly the joint seminar hosted by UCSB in January 2012, with the AIMR returning the favor in February 2013.

Quanta of information

In September this year, the AIMR organized a workshop to deepen their new alliance with the University of Chicago. "The AIMR is thrilled to enter into its first international partnership with the University of Chicago and to strengthen its relationships through the workshop," says Kotani, who opened the session. Throughout the two-day event, chemists, physicists, mathematicians and materials scientists deliberated on a host of topics, including the quantum manipulation of matter, energy harvesting and storage, and the mechanics of breathing.

Among the presenters at the meeting was Shin-Ichi Orimo, a principal investigator at the AIMR, who highlighted the stable and fast conduction properties of lightweight complex hydrides, which could be exploited for hydrogen storage as well as in lithium rechargeable batteries. Also, Ka Yee Lee, a professor at the University of Chicago, shared her research on lung surfactant, a lipid and protein complex that coats the alveoli and eases breathing by reducing surface tension. Her research could help to improve the design of artificial lung surfactants to treat diseases characterized by surfactant deficiency.

"The inaugural workshop highlighted a variety of emerging research opportunities where we hope to develop productive collaborations with our colleagues in Sendai, driven by young researchers from both institutes," says Awschalom, who is now taking spintronics into the realm of quantum information engineering. Awschalom was one of six participants from the University of Chicago who traveled to Japan to exchange ideas with six counterparts from the AIMR.

Also from the University of Chicago, Professor Andrew Cleland discussed his latest successes in harnessing quantum-mechanical phenomena for the development of nanomechanical systems and devices. Cleland's team was the first to construct a machine whose movement followed the peculiar laws of quantum mechanics, previously only observed in nanoscopic particles. By coupling optical, mechanical and microwave electrical signals, Cleland and Awschalom could bring us closer to high-speed quantum communications and long-term storage of quantum information.

"The diversity and breadth of subjects covered at the workshop are an asset to our understanding and utilization of materials and phenomena at the nano- and molecular scale," says Ohno from the AIMR. "I am fully convinced that this and following meetings will lead us to new directions and discoveries." Ohno's confidence is reinforced by the tangible successes that the AIMR has thus far achieved through its joint research centers, whether in Santa Barbara, Cambridge or Beijing. ■

TOP-LEVEL INTERVIEW

Published online on 27 October 2014

The AIMR's reforms positively impact Tohoku University

The various reforms introduced by the AIMR have assisted Tohoku University in its quest to become a world-leading university

Since its establishment in 2007 as a research institute in the Japanese government's prestigious World Premier International Research Center Initiative (WPI), the AIMR has undertaken several reforms, which have helped it become one of the world's leading materials research institutes. Tohoku University is very appreciative of the AIMR's efforts and is now adopting the AIMR's reforms to help it make a further leap forward. President of Tohoku University, Susumu Satomi, and AIMR Director Motoko Kotani discuss the outcomes of these reforms and their impact on the whole university as well as the future expectations of the university for the AIMR.

AIMR Director Motoko Kotani (right) and the president of Tohoku University, Susumu Satomi (left), discuss the positive benefits that the AIMR reforms have had on the university.

Effect of system reforms

Satomi: Since its establishment, our university's philosophy has always been to put research first, to maintain an open-door policy, and to emphasize practice-oriented research and education. As academia becomes increasingly global, Tohoku University needs to flexibly reform systems while maintaining our long-standing tradition in a bid to become a world-leading university. Since being appointed president in 2012, I have set two goals, namely achieving world-class status and spearheading the restoration of Tohoku and Japan after the Great East Japan Earthquake in March 2011. I announced the seven-point "Satomi Vision" to achieve these goals, which stresses the importance of system reforms.

Kotani: First, I would like to mention the introduction of a top-down system for making decisions. Unlike most Japanese universities, where decisions are generally made at faculty meetings, in the AIMR the director can make decisions at his or her discretion, enabling the institute to respond flexibly and rapidly. Since being appointed director in 2012, I have been trying to achieve breakthroughs by promoting collaborations between researchers in the fields of mathematics and materials. We are already seeing accelerated integration of different research fields and benefits over a short timescale as a result of this top-down decision making.

I also want to stress the reforms to the administrative division. In the past, I found it difficult to implement reforms due to red tape. But the AIMR's administrative staff strongly desire to change the university, and they conduct their own work while implementing necessary reforms and supporting researchers. They established their own systems for inviting foreign researchers and organizing international symposiums, which had previously been done by researchers. This enables us to operate smoothly as an international research institute.

Satomi: In July 2014, Tohoku University set up the Organization for Advanced Studies (OAS), which will promote the internationalization of the university and its world-class advanced research. We plan to make the AIMR the first member of the OAS, and then allow other institutes to join. Furthermore, we will create a research reception center at the OAS by taking advantage of the knowledge that the AIMR has accumulated. The establishment of the OAS is the biggest outcome that the AIMR's reforms have brought to our university.

Kotani: Thank you very much. I am very gratified to know that our efforts have brought concrete outcomes and have contributed to the further development of the university.

Reforms to personnel regulations

Kotani: One of the AIMR's missions as a WPI research institute was to recruit outstanding researchers from around the world. To achieve this, we had to offer high levels of compensation. In light of the intensifying global competition in recruiting researchers, I felt strongly that we would be unable to conduct top-level research and attract excellent researchers and students unless we provided them with more incentives than previously.

The AIMR first established a merit-based pay system based on annual appraisals and achievements of researchers in an effort to raise their motivation levels. AIMR researchers can negotiate all sorts of conditions, including payment and research environment. I think that this system is one reason why the AIMR is successful. We have also introduced a joint appointment system, in which excellent researchers affiliated with other departments at Tohoku University and other institutions can concurrently serve as principal investigators at the AIMR.

The Research Support Center provides analytical equipment and English services to support researchers.

Satomi: Traditionally, Japanese universities have not set salaries based on the achievements of researchers. Tohoku University has introduced a distinguished professor system modeled on the AIMR's pay system; it allows high-level professors to receive salary bonuses. Tohoku University must lead other universities by taking advantage of the joint appointment system. We have formed a project team to discuss how to become a hub of the global circulation of talented researchers.

Provision of English research support

Kotani: Providing research support in English was another important mission as a WPI research institute. This was mostly realized in the early stages of establishing the AIMR. Over 90 per cent of our administrative staff can speak Japanese and English, and daily announcements and information about grant applications are provided in both languages. In addition, we have established a system that allows all researchers, including non-Japanese speakers, to easily perform various administrative procedures.

One reform I have undertaken since becoming director was establishing the Research Support Center. The center provides fundamental analytical equipment that is used by most researchers. Staff with a PhD provide support in English, allowing researchers to commence fully fledged research immediately on arriving at the AIMR.

Satomi: Administrative support in English is also essential for Tohoku University to become a truly international university, and I'm thankful to the AIMR for heralding the move. The impact is spreading across the university as some of the AIMR's administrative staff have moved to other departments.

Kotani: We have recently started sharing our administrative expertise with other departments of the university. Examples include secretarial manuals and examples of emails when communicating with overseas research institutes and researchers. We are doing our very best to contribute to the university.

The AIMR created a common space with the aim of promoting interaction between researchers.

Leaping ahead

Kotani: We have implemented many other reforms in addition to those we have discussed. For example, we have created a common space that all of the AIMR staff and researchers can use freely with the aim of fostering interaction between them. Such an open atmosphere was difficult to establish when traditional Japanese culture prevailed, but we consider it to be an essential element for progressing research. We use the space for various events, such as Tea Time every Friday and research presentations and seminars by guest researchers to strengthen interactions. The resulting connectivity has already proved effective for driving collaborative research.

Satomi: Finally, I would like to mention that, in addition to the system reforms, the AIMR has also greatly contributed to the university educationally. We are currently establishing a graduate school that specializes in spintronics — an area where Tohoku University leads the world — thanks to the advanced research at the AIMR and the global connections of its researchers. I am very grateful for that. By actively adopting successful reforms of the AIMR, Tohoku University will continue to become a world-class university and function as a hub for international talent.■

INTERNATIONAL WORKSHOP

Published online on 26 January 2015

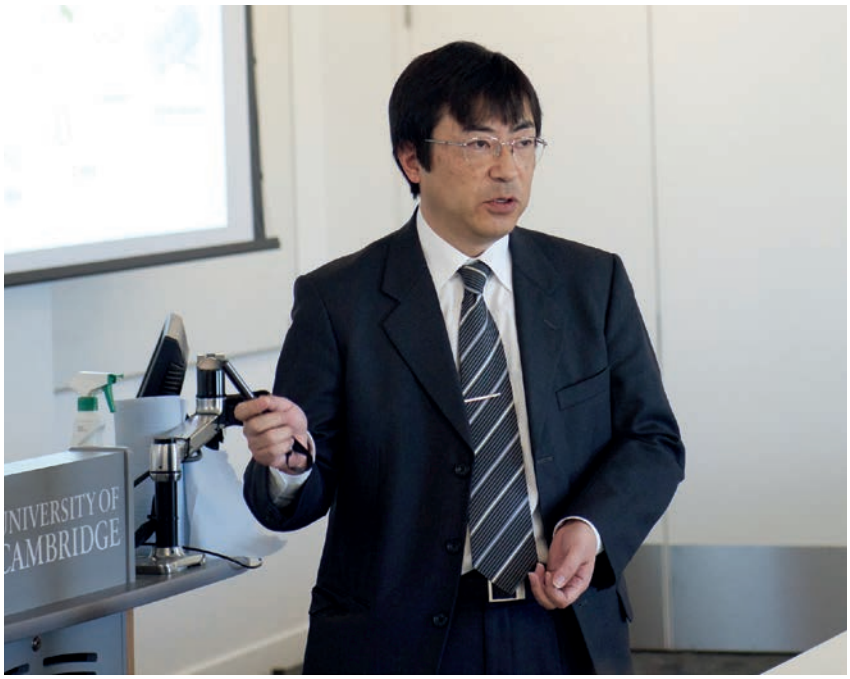
Reinforcing a strong and fruitful friendship

The third workshop jointly organized by the AIMR and the University of Cambridge reinforced the two institutes' longstanding partnership

In early December, the Advanced Institute for Materials Research (AIMR) and the University of Cambridge held a joint workshop in the UK to share their latest discoveries, encourage student exchange and reinforce longstanding partnerships. The event saw presentations on the catalyzing properties of sponge-like nanoporous gold, explorations into the atomic landscape of perovskites and a mathematician's take on materials science.

On the morning of December 9, Susumu Satomi, president of Tohoku University, and Jeremy Sanders, pro-vice-chancellor for institutional affairs at the University of Cambridge, signed a declaration of intent to deepen academic and research collaboration between the two universities. The signing ceremony was attended by AIMR Director Motoko Kotani together with a representative from the Embassy of Japan in the UK and several professors with expertise in the areas of global safety and materials science. More than 40 individuals were present for the program.

The two universities established an AIMR Joint Center (AJC) back in 2012. "In the few years that the center has been operational, it has really developed into a focal point for promoting and strengthening AIMR's presence in Cambridge," says Katherine Orchard, a researcher at the AJC who spends most of her time in Erwin Reisner's laboratory at the Department of Chemistry in Cambridge. Orchard is focusing on the development of nanostructured materials that can absorb solar energy and their use to split water into its constituent elements, hydrogen and oxygen, ultimately paving the way for hydrogen-powered vehicles and electrical devices. "Both the University of Cambridge and the AIMR are recognized as world-class institutions and knowledge transfer between the two can only lead to better research," she adds.



Naoki Asao, a professor at the AIMR, presented his work on nanoporous gold at the third annual AIMR–University of Cambridge joint workshop.

On the day after the official signing ceremony, Orchard joined more than 50 students and researchers at the workshop on December 10 to listen to plenary lectures and discuss the latest trends and controversies in areas such as metallurgy, spintronics and topological insulators.

A parallel session was held to discuss opportunities for student and research exchange between the AIMR and the University of Cambridge. Representing the AIMR, Administrative Director Masaru Tsukada delivered a presentation on the Global Intellectual Incubation and Integration Laboratory (GI^3 Lab), a unique research exchange program in which excellent young researchers are brought to Sendai and hosted at the AIMR for one to three months.

Catalyzing effects

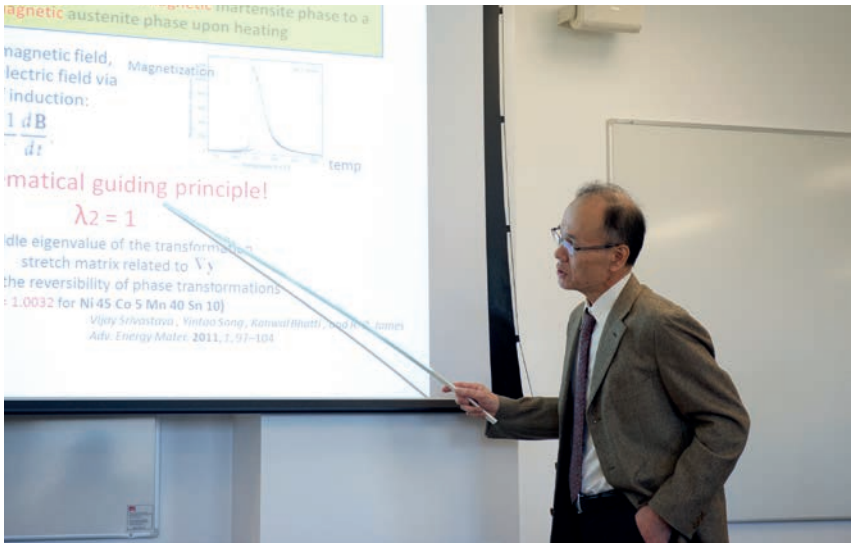
Among the presenters at the scientific sessions was Naoki Asao, a professor at the AIMR who has previously collaborated with Reisner's laboratory in the development of water-splitting systems. Asao shared his work on the use of nanoporous

Over 50 students and researchers attended the joint workshop to listen to talks on various subjects, including the presentation on batteries and supercapacitors by Clare Grey, a professor at the University of Cambridge's Department of Chemistry.

gold for novel, selective chemical transformations, resulting in the production of a variety of valuable organic molecules in a more environmentally sustainable way than existing methods.

Almost a quarter of a century ago, scientists discovered that the synthesis of nanosized particles of gold transformed the catalytically inert metal into a remarkable agent for change. However, these nanoparticles tend to huddle back together into larger particles, losing their catalytic powers. Now, Asao and his colleagues have discovered that nanoporous gold materials, riddled with tiny holes between 10 and 50 nanometers in diameter, have durable structures and high catalytic activity and can be recovered for reuse, thus making them ideal catalysts for synthetic chemistry.

In another presentation, Taro Hitosugi, an associate professor in the AIMR Materials Physics Group, elaborated on the use of scanning tunneling microscopy to closely observe oxide thin films with perovskite structures and potentially engineer their growth, atom by atom. These materials exhibit the fascinating properties of high-temperature superconductivity and magnetoresistance.



Mathematician and professor at the AIMR, Yasumasa Nishiura, was invited to speak on the happy union between mathematics and materials science.

Mathematician and professor at the AIMR, Yasumasa Nishiura, reminded the audience of the historical rapport between representatives in the fields of mathematics and materials science. He went on to elaborate on the potential for mathematics to describe amorphous materials that lack a repetitive atomic structure, such as glass, for which no reliable model exists.

To further foster the close relationship between these two fields of intellectual endeavor, Nishiura's Mathematics Unit has set up a research group with the experimental laboratories of Lindsay Greer at the University of Cambridge and Tadafumi Adschiri at the AIMR and is beginning to extend these links to mathematics departments at Cambridge. "Today's scientific activities are becoming more and more borderless," says Nishiura, "and consequently, joint research centers are important to support the exchange of information and people, especially for theoretical sciences like mathematics."

"The success of the workshop at Cambridge proved that the AIMR Joint Research Center is an important asset for advancing research in the field," says a pleased Kotani. "I am happy that these efforts helped to strengthen the relationship between Tohoku University and the University of Cambridge and anticipate further acceleration in research and more international recognition." ■

Advanced Institute for Materials Research
Tohoku University