AiM Research

RESEARCH HIGHLIGHTS 2016

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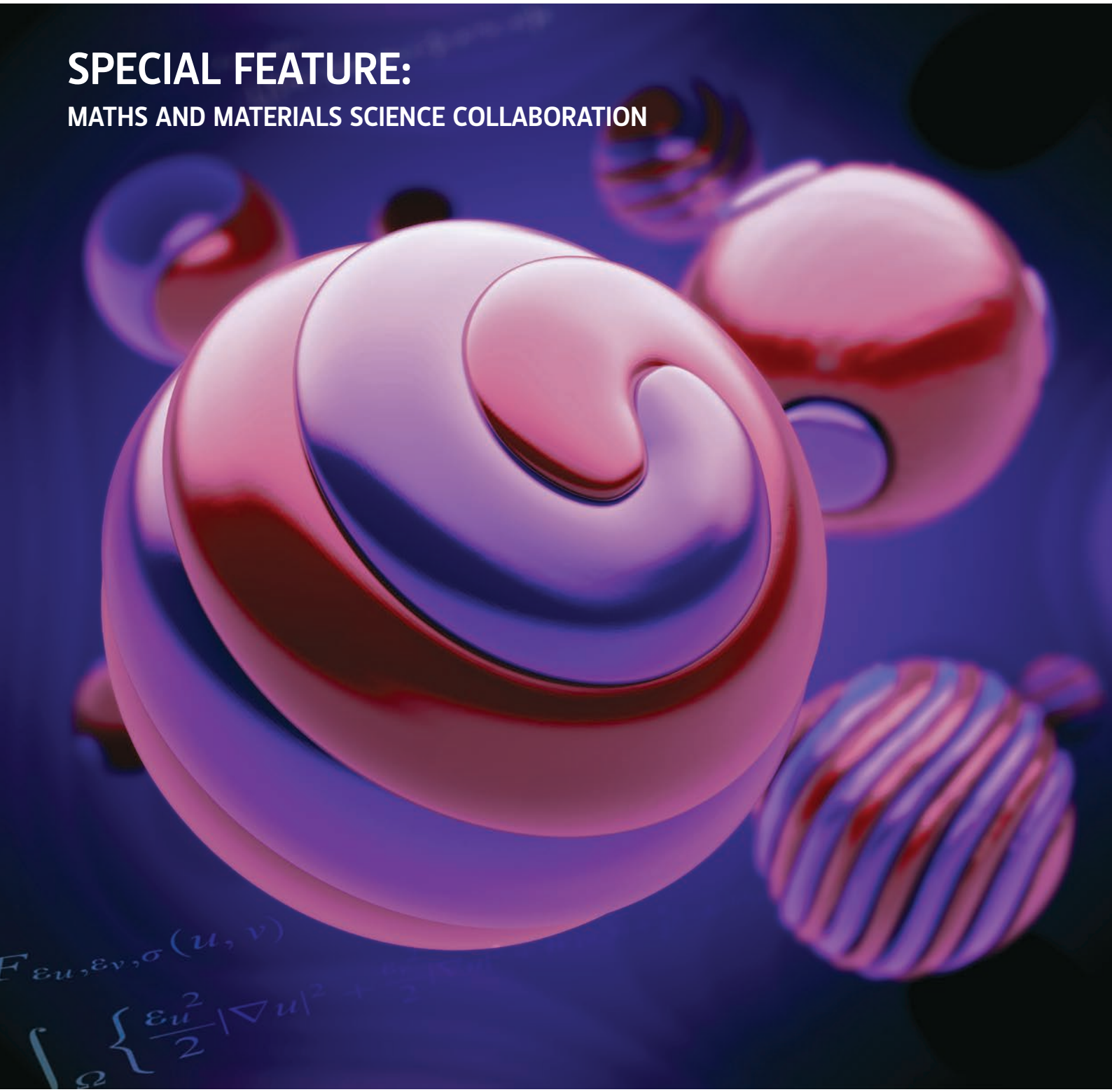

SPECIAL FEATURE:

MATHS AND MATERIALS SCIENCE COLLABORATION

AIMR

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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 — Materials Physics, Non-equilibrium Materials, Soft Materials, Device/System — and the Mathematical Science Group.

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 about 140 leading researchers, around half of whom come from abroad, including 31 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.

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MESSAGE FROM THE DIRECTOR

Past decade lays foundation for new materials science

2017 marks the tenth anniversary of the Advanced Institute for Materials Research (AIMR). The institute was established in 2007 with the support of the World Premier International Research Center Initiative (WPI) program of the Japanese Ministry of Education, Culture, Sports, Science and Technology (MEXT), which seeks to create world-class research centers in Japan. Over the past decade, the AIMR has consistently pursued top-level research in specific areas of materials science and striven to create new materials science.

As a global center for materials science, a defining feature of the AIMR has been the close collaboration between mathematics and materials science. By describing the very broad scope of materials science in the universal terms of mathematics, researchers at the AIMR are trying to uncover commonalities between various materials and so create new research topics and results. This bold attempt to team up mathematicians and materials scientists is unique in the world and epitomizes AIMR's position at the cutting edge of materials science research.

In publishing this edition of *AIMResearch* on the occasion of the institute's tenth anniversary, we have included a special feature that focuses on fusion research in mathematics and materials science. In it, we introduce research results that characterize the last decade of AIMR's outputs.

While immersed in such front-line research, AIMR has also spent the past year actively engaged in exchanges with international researchers and research institutions and across different fields of materials science. The AIMR International Symposium 2016 (AMIS2016) convened in February 2016 and featured 22 invited speakers, including Alexander Mikhailov, a theoretical scientist at the Fritz Haber Institute of the Max Plank Society, and Akira Fujishima, a chemist and president of Tokyo University of Science. The symposium was attended by more than 230 researchers in every field of materials science, from 14 countries. In May, the AIMR also joined other WPI centers in attending the 2016 Spring Meeting of the European Materials Research Society (E-MRS), convened in Lille, France.

In a new development that seeks to connect basic research with society, the AIST-Tohoku University Mathematics for Advanced Materials Open Innovation Laboratory (MathAM-OIL) was established in July to promote data-driven materials science. AIMR researchers from Tohoku University are already active in the laboratory, advancing research in mathematics, computational science, theoretical physics, theoretical chemistry and materials science to accelerate materials development and the application of research to industry.

Having established a firm foundation in its first decade of activity, the AIMR is entering a new phase in which it seeks to generate novel materials science. We would like to take this opportunity to express our thanks to all our supporters. We at the AIMR will continue to advance high-quality research, act as a hub for international brain circulation, and contribute to the development of global materials science and society.

Motoko Kotani
Director
AIMR

Published online on 30 January 2017

INTERVIEW WITH A MATHEMATICIAN

Experimenting with maths and materials

Yasumasa Nishiura gives a mathematician's perspective on the five-year collaboration between mathematics and materials science at the AIMR

What happens when you bring mathematicians and materials scientists under one roof? The Advanced Institute for Materials Research (AIMR) at Tohoku University is five years into a bold experiment that uses mathematics to glean insights into materials. AIM*Research* talks to Yasumasa Nishiura — an applied mathematician and unit leader of the AIMR's Mathematical Science Group — about the unexpected results from the AIMR's radically new way of thinking.

AIM*Research*: What unique perspective does mathematics bring to materials science?

Nishiura: The language of mathematics brings new concepts and viewpoints to the understanding of materials science. Without it, some material properties cannot be described explicitly.

Mathematics is also a very powerful way to overcome rigid and obsolete conceptual frameworks. A typical example is chaos theory, a field of study in mathematics that tries to predict the unpredictable. Chaotic systems behave in unexpected ways and yet are entirely controlled by their initial conditions. About half a century ago, nobody knew about this concept of chaos, so they just threw data away because it was too 'noisy' and didn't contain any definable structures. But today, researchers recognize that even very noisy-looking data sometimes have internal structures that contain extractable information. To do that, they need mathematical concepts like chaos. Otherwise, they're just wandering in the dark.

AIM*Research*: What are some interesting results that have come out of combining materials science and mathematics at the AIMR?

Nishiura: We have applied concepts in the well-established mathematical field of topology, which studies the twists and turns of shapes, to materials science. Topology offers a new framework for understanding amorphous structures that lie between the perfectly ordered arrangements of crystals and random structures like liquids. More specifically, we have used an analytical technique for uncovering geometries hidden in large data sets, called persistent homology, to analyse structures that nobody has succeeded in characterizing, and to pin down the definition of the term amorphous.

Related to topology is an emerging field in materials science known as spintronics. Conventional electronics uses electrons to carry energy and information. In contrast, spintronics relies on electron spin. Many aspects of spintronics can be explained by a mathematical framework used to study very advanced geometries known as K-theory. Take, for example, promising materials in the field of spintronics known as topological insulators, which are insulators on their inside but conductors on their surface. K-theory can clarify why this phenomenon is so robust in topological insulators.

An applied mathematician by background, Yasumasa Nishiura is excited about the collaboration between materials scientists and mathematicians at the AIMR and believes that it is a two-way process that can lead to advances in both disciplines.

Another area I am deeply involved in is self-organization processes. A standard way of fabricating nanomaterials is from the top down — gradually chipping away at a solid block using techniques such as nanolithography. The alternative approach starts from the bottom up — constructing something from nothing. Self-organization is one such technique, in which basic building blocks are left to spontaneously form larger building blocks. It lets nature do its work. In materials science, self-organization is a fertile but undeveloped area. My work specifically involves confining polymers that are extremely averse to each other in very tiny spheres. The polymers seek to decrease the free energy and, in the process, form interesting patterns. We have developed a qualitative mathematical model that can be used to control the size and morphologies of the patterns that pop up, which has wide applications including in the medical sciences. For example, structured particles could be used to test immunity by employing reactions between antibodies and antigens.

Finally, we have applied a mathematical discipline known as discrete differential geometry to explore the design of

carbon structures. Discrete differential geometry structures contain a distinct number of elements, such as atoms. We have used its concepts to make many interesting structures from carbon atoms, such as large carbon cages with 20-sided polyhedrons. We have even placed molecules inside these cages.

AIM*Research*: Can mathematicians also learn from materials scientists?

Nishiura: Yes, collaboration is not just one way; it goes both ways. We mathematicians often get very fresh and intriguing feedback from experimentalists. This is quite new for us and has led to the generation of new mathematics, or at least the discovery of new problems.

At the AIMR, such two-way feedback is greatly accelerated. For example, we have explored together the dynamical evolution of material structures, which demands generalizing the concept of persistent homology in space and time. We sit very close to each other and work together in one building. As far as I am aware, the AIMR is the only institute in the world where this happens in materials science.

AIM*Research*: What are some challenges you face?

Nishiura: Overcoming cultural differences is not easy. Mathematicians and materials scientists have different answers to questions about what the important and interesting aspects of a problem are and what they value most. They also have very different styles of working. Experimental laboratories are more hierarchical in structure and require a lot of space and money since they need expensive facilities and large teams of technicians. But mathematicians are more private. We like to discuss, but we also need periods of solitude. At the AIMR, we have been given the time to warm up to each other.

AIM*Research*: What policies has the AIMR introduced to facilitate this collaboration?

Nishiura: Five years ago, we set ourselves three main targets: non-equilibrium structures, topological structures and hierarchical structures. A healthy mix of materials scientists and mathematicians work together to achieve these goals.

Nishiura is researching the maths of self-organization processes and how it can be applied to synthesize new materials through bottom-up approaches.

We also established the Interface Unit, a group of researchers who act as free electrons, with the freedom to choose which projects they want to get involved in. They are young and ambitious — younger people tend to be more flexible and curious.

Another characteristic of the group is its heterogeneity. The researchers have backgrounds in applied mathematics, physics, statistics, information science, computer science and modeling, as well as physical and theoretical chemistry. This is important because you don't know *a priori* what tools or methodologies will be important in materials science. Heterogeneity catalyzes serendipitous discoveries.

AIM*Research*: What areas do you expect the AIMR to further develop in the coming years?

Nishiura: Experiments today generate huge amounts of data, which has fueled an entire field of science devoted to extracting knowledge from large data sets. Traditionally, this has involved processing information using statistics, computer science and information technology. In materials science, this approach is characterized by the popular phrase materials informatics. Mathematics can help to explain how these information processing systems work.

AIM*Research*: Could the AIMR model be applied to other fields besides materials science?

Nishiura: Yes. That is the most important message that the scientific community should take from the AIMR. In just five years, we have become extremely successful. Our success springs from the nature of mathematics. Since mathematical methods treat only the relations between objects and are independent of material properties, they have great potential to be applied to other disciplines besides materials science. The AIMR is a sort of trial for what happens when you inject mathematics into materials science. We have formed some interesting collaborations and obtained some interesting results. So why not try injecting mathematics into other disciplines? ■

ROUNDTABLE INTERVIEW

Published online on 26 September 2016

A mathematician, an experimentalist and their interpreter

By pooling their unique perspectives, three AIMR researchers with very different backgrounds have used a powerful new mathematical technique to discover structures lurking in amorphous solids

Remarkable things happen when researchers get together to explore new territories at the margins of their disciplines. This is an approach that the AIMR at Tohoku University has been actively pursuing in recent years at the border between mathematics and materials science.

In 2010, a seminar held at the AIMR spawned discussions between a mathematician, an experimentalist and a physicist. Six years later, this initial discussion has blossomed into groundbreaking findings in an emerging area of mathematics known as persistent homology, with the three researchers able to characterize the underlying atomic order of a class of materials having mostly random structures. Until now, this order had remained elusive to scientists using conventional methods.

Inspired by a former supervisor, Yasuaki Hiraoka is a mathematician interested in applying mathematics to materials science and, in the process, generating new mathematics.

An adventurous mathematician

For a mathematician, Yasuaki Hiraoka certainly has an unconventional resume: he started off studying electrical engineering at Osaka University and now works at a center for materials science — the AIMR. He is passionate about exploring the interface between mathematics and applied sciences. Hiraoka first learned that there could be more to a career in mathematics than abstract thought from his master's supervisor, Yuji Kodama, who is now a professor at The Ohio State University. "He's my inspiration in that he does serious mathematics — he's a pure mathematician — but he's also famous in the field of optical communications," Hiraoka says. "I wanted to become like him."

Hiraoka is not just interested in applying mathematics to real systems; he also works in the opposite direction — using applications to generate new mathematics. "I'm eager to develop my own mathematics," he says.

These interests explain why Hiraoka is so enthralled by the emerging field of persistent homology — a powerful mathematical framework that can uncover patterns buried in large sets of data. First developed at the beginning of the twenty-first century, persistent homology has taken off in recent years, finding applications in fields as diverse as neuroscience, linguistics, particle theory and artificial intelligence. Hiraoka considers it a tremendously exciting time to be working in the field.

The power and versatility of persistent homology lie in its ability to mathematically express the multiscale organization so often observed in natural phenomena. For example, before coming to the AIMR, Hiraoka used persistent homology to explore the structures of bioproteins, and, in particular, used it to link the structure of a protein to how compressible it is.

Today, Hiraoka heads a group at the AIMR that is leading the charge in applying persistent homology to materials science. "We are the only group in the world seriously applying persistent homology to materials," he says.

Hiraoka had just finished writing a book on the subject when the AIMR invited him to speak at a seminar. It was there that he first met his future collaborators, Akihiko Hirata and Takenobu Nakamura.

An experimentalist and an interpreter

Akihiko Hirata is the experimentalist of the trio. His interest lies in using analytic techniques such as electron diffraction and transmission electron microscopy to probe the atomic structures of so-called amorphous materials such as bulk metallic glasses and other glasses. Unlike crystalline materials, these glasses do not have periodic arrangements of atoms or molecules, which makes experimental analysis of them far from straightforward. Their disordered structures produce blurry diffraction patterns and complex micrographs, which are extremely challenging to glean meaningful structural information from. To make sense of the data, Hirata needed to consult with a mathematician familiar with persistent homology — Hiraoka's visit offered the perfect opportunity.

It was not the first time that Hirata had collaborated with a mathematician. Together with mathematician Kaname Matsue (then an assistant professor at the

Akihiko Hirata (left) is an experimentalist who uses powerful analytical techniques to explore amorphous materials. He is very appreciative of the help from Takenobu Nakamura (right), a physicist who helps interpret mathematical terminology and concepts into physical ones and vice versa.

The trio discussing the application of persistent homology to amorphous materials.

AIMR), Hirata had previously explored the structure of metallic glasses using an angstrom-beam electron diffraction technique he helped develop, which uses an electron beam only several atoms thick to obtain diffraction patterns. They produced the first experimental evidence for order with the same symmetry as a 20-sided polygon (icosahedron) in metallic glasses. "It was a great, fresh experience for me," says Hirata of the study published in *Science* in 2013[1]. "I was inspired by mathematicians."

Interpreting between the two worlds comes naturally to Takenobu Nakamura, a physicist who understands the terminologies used by mathematicians and experimentalists. He has honed his interpretive skills through studying subjects heavy in mathematics, such as statistical physics and non-equilibrium, nonlinear physics.

At the AIMR, Nakamura works as a researcher in the Interface Unit, which serves as a bridge between materials scientists and mathematicians. Even with that background, it still takes him some time to become proficient enough to tackle a new project. "The first thing I do is learn both terminologies by making a translation table for the two fields," he says. "Then we can start the conversation."

Persistence pays off

Seeing the potential of using persistent homology to characterize the structure of amorphous solids, the trio began establishing common ground. Nakamura's experience proved invaluable in this endeavor. "Before seriously starting this work, we took several months just to set up a common terminology and frame of reference," says Hiraoka. "We wanted to find our 'sweet spot.'"

Working together, the three researchers eventually discovered that they could use a special diagram based on persistent homology — known as a persistence diagram — to visualize the structure of amorphous solids. Curves in a persistence diagram indicate the presence of local structures. The researchers demonstrated this for pure glass and found that it contains different ring-like configurations of atoms (see related highlight on page 6). "The first time we found this curve, we knew it was what we had been searching for," says Hiraoka. Such structures had never been seen before in glass. The results were published in *Proceedings of the National Academy of Sciences USA* in June 2016[2]. "I don't think any two of us working together could have obtained this result," says Hiraoka. "It took all three of us."

More importantly, the approach demonstrated the power of persistent homology to unveil structures hiding in the randomness of amorphous solids. The researchers intend to apply this approach to other amorphous materials and to generate new mathematics. "We first focused on silica, but the developed methods are applicable to a wide range of other glass structures," says Nakamura.

A collaborative environment

The finding was also due to the special environment cultivated at the AIMR. The institute has created many opportunities for mathematicians and materials scientists to interact and work with each other through target projects, fusion research, workshops and seminars, including the Target Project–Interface Unit Joint Forum. The culture of exploring the interface between mathematics and materials science is deeply ingrained in the institute's DNA.

Recent successes flowing from this outlook include the synthesis and exploration of belt-shaped 'nanohoops' by Hiroyuki Isobe's team[3]. Various other collaborative studies have led to discoveries in the stoichiometric control of deposited thin films using a stochastic model, formulation of the bulk-edge correspondence of topological insulators based on K-theory, mathematical modeling of periodic structures observed along grain boundaries, as well as the prediction of phase separation morphologies of block copolymers using Cahn–Hilliard equations.

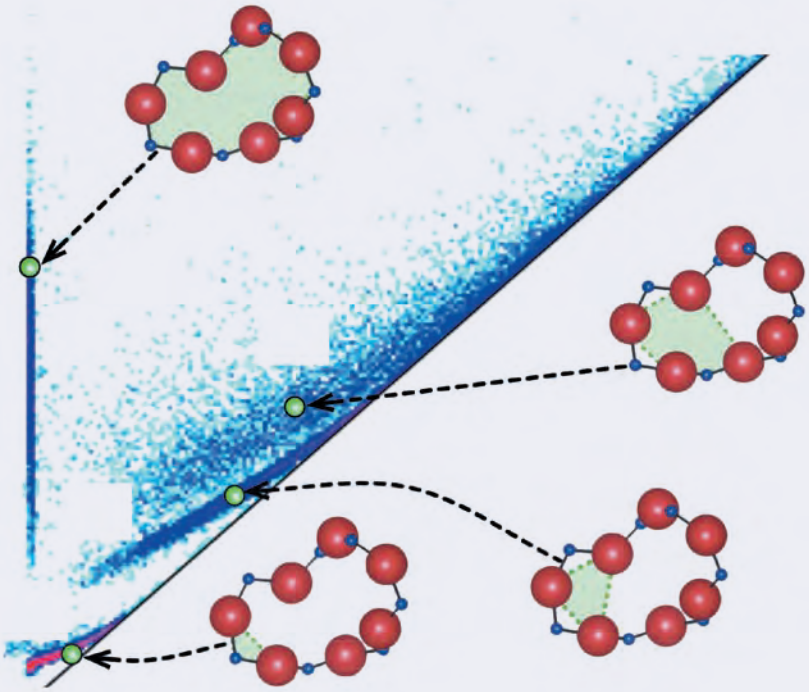
Hiraoka is appreciative of the environment at the AIMR. "Director Kotani allowed me to establish a laboratory, which is really unusual in the mathematics community," he says. "Mathematics is usually done by individuals working alone. But in some cases, it's also good to organize a team to enhance the research field more aggressively. Persistent homology has now become such a field." ■

1. Hirata, A., Kang, L. J., Fujita, T., Klumov, B., Matsue, K., Kotani, M., Yavari, A. R. & Chen, M. W. Geometric frustration of icosahedron in metallic glasses. *Science* **341,** 376–379 (2013).
2. Hiraoka, Y., Nakamura, T., Hirata, A., Escolar, E. G., Matsue, K. & Nishiura, Y. Hierarchical structures of amorphous solids characterized by persistent homology. *Proceedings of the National Academy of Sciences USA* **113,** 7035–7040 (2016).
3. Sun, Z., Suenaga, T., Sarkar, P., Sato, S., Kotani, M. & Isobe, H. Stereoisomerism, crystal structures, and dynamics of belt-shaped cyclonaphthylenes. *Proceedings of the National Academy of Sciences USA* **113,** 8109–8114 (2016).

Published online on 29 August 2016

Persistent homology: Uncovering order in a sea of randomness

A new analytical technique proves to be a powerful method for studying multiscale order in glasses



Structural features in silica glass appear against a random background. The persistence diagram reveals ring-like structures of atoms (red spheres) in silica glass.

By harnessing the power of an emerging mathematical technique known as persistent homology, AIMR researchers have extracted important geometric information about the atomic configuration of the mostly random structure of glasses[1].

Glasses range from window glass made from silica to metallic glasses. In contrast to the periodic atomic order of crystals, the atoms in glasses are largely randomly distributed. But glasses do not have entirely random structures, and their local atomic order can strongly influence their properties. However, characterizing this atomic order in glasses has proved very challenging because the order is largely masked by the overall randomness of glass structure.

Yasuaki Hiraoka of the AIMR at Tohoku University and his co-workers turned to applied mathematics for help. In particular, they explored a recently developed mathematical technique called persistent homology. This powerful analytical method can characterize geometric structures that lie hidden in large sets of data, and it is being applied in a wide range of fields.

"We used persistent homology to investigate one such geometric structure, namely the hierarchical relationship of rings in the atomic configuration of glasses," explains Hiraoka.

Employing a model of the atomic positions of a glass as the input, the researchers used software based on persistent homology to generate a graphical representation of the structure, which is known as a persistence diagram.

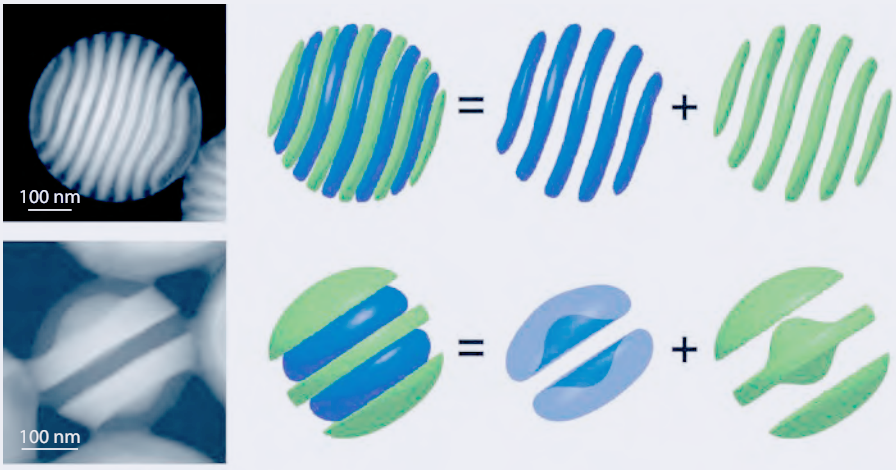
The persistence diagram reveals the presence of local multiscale structures in a material. Depending on geometrical parameters such as the size of the atoms and the distances between them, different ring-like configurations of atoms exist. For a perfectly random structure, no local ring structure is favored and the data background looks uniform. For a crystalline structure, geometric features are preferred and clear structures appear in the analysis. In the case of the silica glass studied, the results are intermediate between these two extremes: a uniform random-like background is observed along with the presence of a few ring-like structures, which are characterized by curves in the persistence diagram (see image).

This ability of persistent homology to uncover hierarchical structures that are hidden to conventional techniques is a powerful demonstration of the potential of this method for studying the structure and properties of glasses and other amorphous materials.

> "Our next target for amorphous structural analysis is to try to mathematically characterize the glass transition."

For the future, the team has set its sights even higher. "Our next target for amorphous structural analysis is to try to mathematically characterize the glass transition — one of the most important problems in current condensed-matter physics," says Hiraoka.

1. Hiraoka, Y., Nakamura, T., Hirata, A., Escolar, E. G., Matsue, K. & Nishiura, Y. Hierarchical structures of amorphous solids characterized by persistent homology. *Proceedings of the National Academy of Sciences USA* **113,** 7035–7040 (2016).



Left: Scanning electron microscope images of experimentally synthesized diblock copolymer structures. Right: Diblock copolymer structures of polystyrene (blue) and polyisoprene (green) generated by a numerical model.

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Block copolymers:

Predicting polymer shapes

A model that accurately predicts the structures of block copolymers is promising for developing designer polymer nanoparticles

By applying a new mathematical approach, AIMR researchers have gained insights into the nanostructures that mixtures of two plastics form under various conditions[1].

Most commercial plastics, or polymers, consist of long chains of one type of molecule. But just as different metals can be combined to produce alloys that have superior properties to their constituent metals, so polymer properties can be tuned by mixing different polymers.

Polymers made up of two types of polymer molecules are known as diblock polymers. The two chains can arrange themselves into a wide range of different configurations as a result of the attractive and repulsive forces acting between them. Even more shapes can be generated by confining diblock polymers to different volumes, such as a sphere or cylinder. This ability to modify the shapes, and hence the properties, of diblock polymers is generating much interest because it holds promise for making tiny chemical reactors and nanoparticles for drug delivery, among other possible applications.

"Understanding the phase behaviors of diblock copolymers in confined spaces is one of the major problems in soft-matter physics," says Hiroshi Yabu of the AIMR at Tohoku University. "Unique structures with separated microphases emerge in three-dimensionally confined spaces. While such 'frustrated phases' have been investigated experimentally and theoretically, little is known about the energetics of such systems."

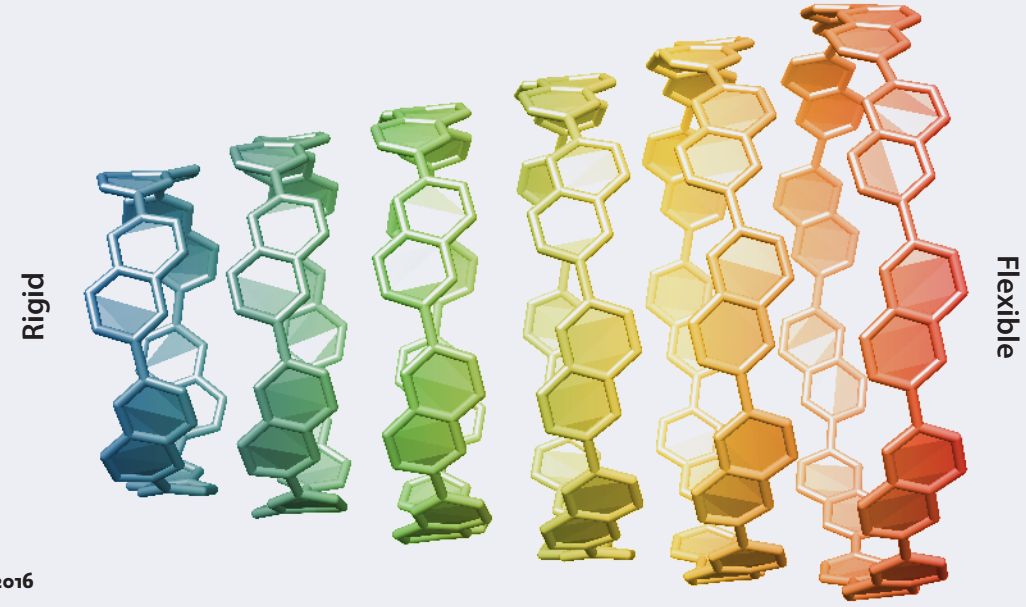
Now, Yabu and co-workers, by building on a previous mathematical analysis[2], have used a set of coupled equations to numerically explore the morphologies and phases of diblock copolymers confined within spheres. They synthesized nanoparticles containing mixtures of the polymers polystyrene and polyisoprene (the polymer of natural rubber). Depending on the conditions used, the researchers obtained a variety of configurations, including some that resembled tennis balls, onion layers or hamburgers. When they compared transmission electron micrographs of diblock copolymers with predictions based on their numerical model, they found that the results were strikingly similar (see image).

"This model, which shows the relationship between the free energies and morphologies of diblock copolymers confined in small particles, has great predictive power and consistency with experimental results," says Yabu. "It provides not only explanations of phenomena, but also reliable guidelines for designing new experiments. In particular, it could be used to suggest how to make new complex morphologies experimentally and be useful for finding new functional materials for applications such as drug delivery.

> **"Understanding the phase behaviors of diblock copolymers in confined spaces is one of the major problems in soft-matter physics."**

The researchers intend to use their model to explore other mixtures of polymers as well as the effect of factors such as the copolymerization ratio and molecular weight.

1. Avalos, E., Higuchi, T., Teramoto, T., Yabu, H. & Nishiura, Y. Frustrated phases under three-dimensional confinement simulated by a set of coupled Cahn–Hilliard equations. *Soft Matter* **12,** 5905–5914 (2016).
2. Teramoto, T. & Nishiura, Y. Morphological characterization of the diblock copolymer problem with topological computation. *Japan Journal of Industrial and Applied Mathematics* **27,** 175–190 (2010).



The larger the nanohoop, the more flexible and less nanotube-like it becomes.

Published online on 31 October 2016

Carbon nanostructures: In the loop

Nanoscale hoops of carbon atoms are poised to reveal the advantages of curved structures

Stronger than steel, lighter than aluminum, more conductive than copper — carbon nanotubes boast some exceptional properties.

One key to these properties is the nanotube's unique shape: a hollow cylinder of tightly bonded carbon atoms, across which a sea of electrons freely flows. To gain a deeper understanding of how the curved shape contributes to the properties of carbon nanotubes, AIMR researchers have synthesized a series of belt-shaped carbon 'nanohoops', which mimic the nanotube structure, but are shorter and simpler[1]. In creating these carbon structures, the team discovered that the nanohoops have a rich chemistry of their own.

Hiroyuki Isobe and his colleagues from the AIMR at Tohoku University made the series of nanohoops by combining flat carbon structures called arylenes. The arylenes join together to form a loop in a process akin to threading flat beads together to form a necklace. Using an approach called random synthesis, the team produced nanohoops ranging in size from six to eleven arylene units.

The researchers showed that the true structural diversity was considerably greater than just six nanohoops of different sizes. Each arylene 'bead' can attach to the growing nanohoop in two possible orientations, forming different structures known as stereoisomers. Teaming up with a mathematician, the researchers calculated the total number of possible stereoisomers that a nanohoop of any given size could have. These calculations predict that the largest, 11-arylene nanohoop can form 126 different stereoisomers.

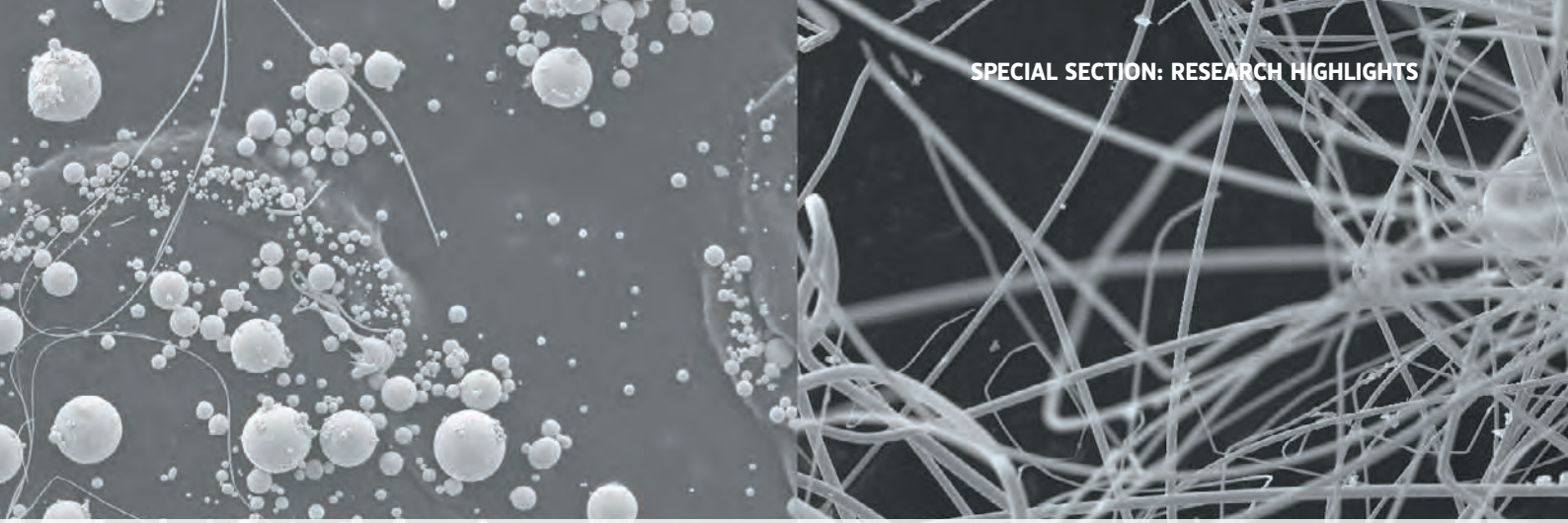
> "We are now trying to reveal the secrets hidden in the persistent cylindrical shape, and hope that many new surprises will enrich the chemistry and its allied areas."

More significantly for carbon nanotube research, the team used variable-temperature nuclear magnetic resonance (NMR) to show that the larger the nanohoop, the more flexible its structure becomes (see image). To be a good model for a carbon nanotube's stiff cylindrical shape, rigid nanohoops are required. Of Isobe's nanohoops, only the smallest, six-arylene nanohoops showed sharp peaks in the room-temperature NMR spectrum, which indicate the necessary rigid cylindrical structure.

"Our study is the first to show this threshold between rigid, cylindrical molecules and fluctuating molecules," Isobe says. The team found that of the many structural variants of nanohoops that have been designed to mimic nanotubes, very few of them successfully mimic the persistent cylindrical shape of carbon nanotubes.

The work lays the foundations for further studying the unique structural chemistry of nanohoops. "This study shows that we are at a very fundamental, early stage of understanding the chemistry of these materials," Isobe adds. "We are now trying to reveal the secrets hidden in the persistent cylindrical shape, and hope that many new surprises will enrich the chemistry and its allied areas."

1. Sun, Z., Suenaga, T., Sarkar, P., Sato, S., Kotani, M. & Hiroyuki, I. Stereoisomerism, crystal structures, and dynamics of belt-shaped cyclonaphthylenes. *Proceedings of the National Academy of Sciences USA* **113,** 8109–8114 (2016).



Published online on 28 November 2016

The structures produced by gas atomization of palladium-based metallic glass depend on a parameter known as the Ohnesorge number: microdroplets (left) form at low values of the Ohnesorge number, whereas nanowires (right) are produced at higher values.

Metallic glasses: Mathematics nails diameter distribution

Mathematical analysis reveals that the threshold between the formation of a wire and a droplet made from metallic glasses hinges on a single parameter

By mathematically analyzing the nanostructures of metallic glasses, AIMR researchers have gleaned new insights into how these useful materials form. This knowledge will help to optimize the manufacturing process.

Metallic glasses are attracting a lot of interest because their disordered structures give them different properties from conventional metals, which have highly ordered structures. In particular, nanowires made from metallic glasses are promising for use in magnetic sensors, fiber-reinforced composites and heterogeneous catalysts.

Koji Nakayama of the AIMR at Tohoku University and co-workers previously demonstrated that metallic glass nanowires can be produced by gas atomization — a common process for the commercial production of metal and alloy powders. In this method, a molten metal is 'atomized' into small droplets by high-speed jets of a chemically unreactive gas. But the complexity of the atomization process makes it difficult to control the sizes and shapes of metallic glass nanowires.

Now, by teaming up with mathematicians at the AIMR, Nakayama's group has statistically analyzed the formation of microdroplets and nanowires made from a palladium-based metallic glass[1]. They found that the forms of the droplets and wires are related to a parameter known as the Ohnesorge number, which relates the viscous forces of a fluid to its surface tension forces. In particular, microdroplets form at low values of the Ohnesorge number, whereas nanowires are produced at higher values (see image).

> "Collaboration with mathematicians was vital because they helped us to develop the statistical models."

The researchers also found that the distribution of nanowire diameters follows a well-known statistical pattern in nature, called the log-normal distribution. "The log-normal distribution is defined as the distribution of a random variable whose logarithm is normally distributed," explains Nakayama. "It has been widely applied for fitting data such as the sizes of organisms, the numbers of species in biology and incomes in economics."

These findings will assist researchers to develop a clearer picture of how nanowires of metallic glasses form during gas atomization, which will eventually lead to better control of the process.

The researchers selected palladium-based metallic glass for the study because of its strong glass-forming ability and high resistance to reacting with oxygen, but Nakayama notes that the same analysis can be carried out on other metallic glasses.

Nakayama values mathematicians' input to the analysis. "The study was done with the support of the AIMR Fusion Research Program, which promotes cross-disciplinary research between materials science and mathematics to gain new insights into industrial products," says Nakayama. "Collaboration with mathematicians was vital because they helped us to develop the statistical models."

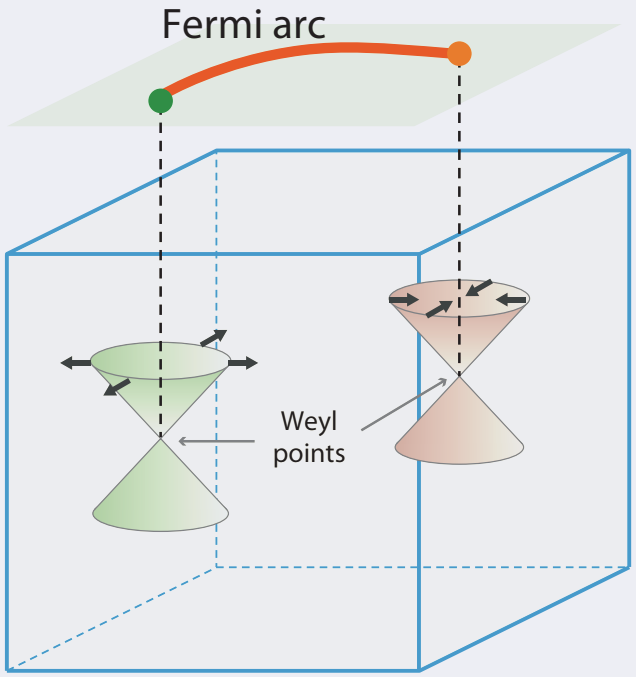
1. Yaginuma, S., Nakajima, C., Kaneko, N., Yokoyama, Y. & Nakayama, K. S. Log-normal diameter distribution of Pd-based metallic glass droplet and wire. *Scientific Reports* **5**, 10711 (2015).

Published online on 26 December 2016

Quantum materials:

Massless particles jump out from a sea of electrons

Tadpole-shaped surface states on metal crystals confirm the presence of exotic quasiparticles ideal for three-dimensional computing devices



Identifying graphene-like Weyl points inside metal crystals by their distinct surface Fermi-arc patterns could help usher in ultrahigh-speed electronics (the thick black arrows indicate the spin direction).

An elusive quantum state that can polarize charge carriers for spintronic applications and move them, undisturbed, at ultrahigh speeds has been directly observed by a team at the AIMR[1].

First predicted in 1929 but only observed in 2015, Weyl fermions are a special class of quantum particle that have the same spin properties as electrons but are massless, like photons. This combination enables electronic charges to be transported at much higher speeds than possible in today's computing devices. It also allows the quasiparticles to effortlessly move past defects in a crystal structure instead of being scattered by them.

Researchers, however, were unable to spot Weyl fermions until the recent discovery of 'semimetals' made from binary transition metals. These materials split electrons into pairs of Weyl fermions at points in the crystal lattice where empty conduction bands cross over into electron-containing valence bands. At these crossover points, Weyl semimetals exhibit properties analogous to a three-dimensional form of graphene but with valuable spin-polarized bands absent in atomic carbon sheets.

Calculations suggest that several types of Weyl semimetals can exist. Now, Seigo Souma from the AIMR at Tohoku University and colleagues in Japan and Germany have made it easier to identify materials with these technologically exciting properties. Souma explains that Weyl fermions always appear with a definite handedness, or chirality. This property is manifested by surface states that have unusual shapes such as those resembling a tadpole or a dog bone. But spotting these 'Fermi-arc' states is challenging and time consuming since metals contain many surface states.

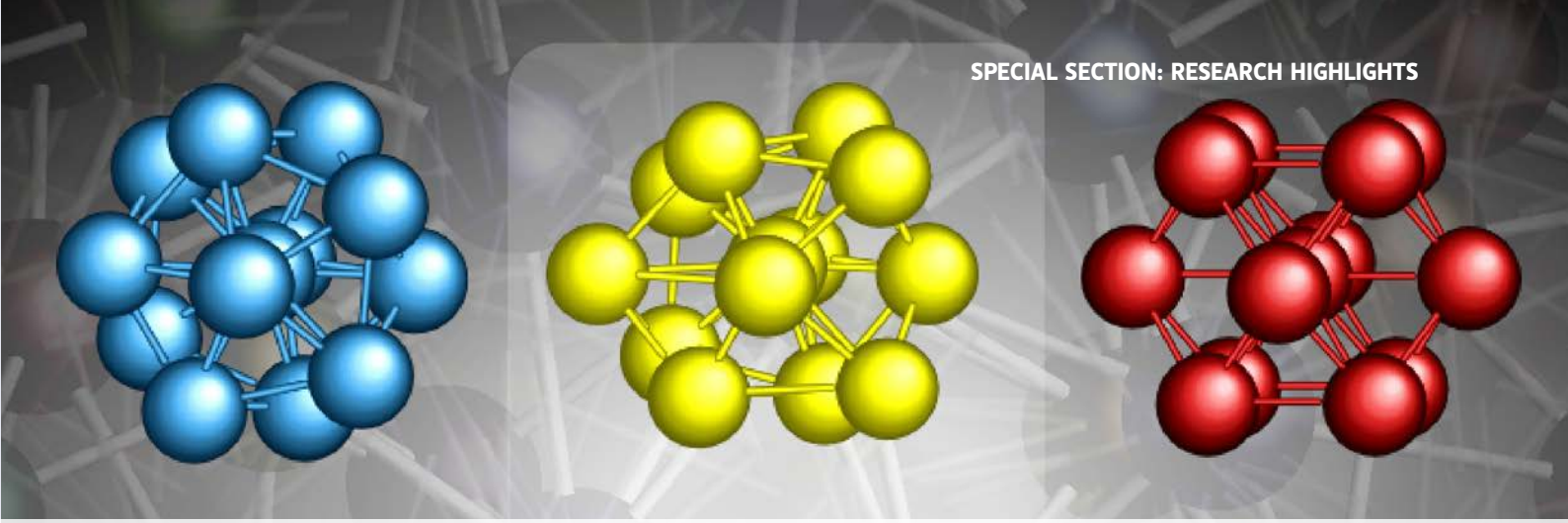
> "These particles are superior to graphene in several ways and can handle large currents because they're so robust."

"It's necessary to use band calculations to assign Fermi-arc states from the many observed surface bands," says Souma. "Without performing these computations, you normally can't see which is which."

To detect Fermi-arc states purely by experiment, the AIMR team investigated a niobium–phosphorous material reported to have an ultrahigh charge mobility and large magnetic forces. The team realized that cleaving this metal along specific lattice orientations could produce thin crystal sheets with niobium exposed on one side and phosphorous on the other. By measuring the electronic states of each side with photoemission spectroscopy and contrasting the differences, they mapped the Weyl crossover points and the branch-like Fermi-arc states connecting them (see image).

"No matter how much the surface potential deforms Fermi-arc states, the Weyl points never move," explains Souma. "These particles are superior to graphene in several ways and can handle large currents because they're so robust."

1. Souma, S., Wang, Z., Kotaka, H., Sato, T., Nakayama, K., Tanaka, Y., Kimizuka, H., Takahashi, T., Yamauchi, K., Oguchi, T. *et al.* Direct observation of nonequivalent Fermi-arc states of opposite surfaces in the noncentrosymmetric Weyl semimetal NbP. *Physical Review B* **93,** 161112(R) (2016).



Published online on 26 August 2013

The assumed icosahedral local atomic structure of metallic glasses (left, blue), the face-centered cubic (fcc) structure of the corresponding metal crystal (right, red) and the actual distorted icosahedral arrangement of metallic glasses (center, yellow). The top and bottom rows show the same structures from a different angle.

Metallic glasses: All in order

The local atomic order of metallic glasses has been solved by electron-beam imaging at the atomic scale

Most of the glasses that we encounter everyday are transparent and appear to be rather ordinary. A closer look, however, reveals an intriguing composition: glasses are basically frozen liquids, meaning that their atoms are randomly arranged. Researchers from the AIMR at Tohoku University and international collaborators have now shown that, surprisingly, the atoms of some glasses containing metallic components also display a local order that is based on icosahedral geometric structures[1]. "We provide the first direct experimental evidence of the existence of icosahedral order in metallic glasses," explains Mingwei Chen, who led the research team to this discovery, which confirms previous theoretical predictions.

Atoms in metals behave like perfect spheres, forming perfect crystals with atomic arrangements in the form of face-centered cubic (fcc) or body-centered cubic (bcc) structures, for example. Some metallic compounds can also form glasses when cooled fast enough after melting. Scientists were unsure as to why some metals form glasses instead of crystallizing and assumed that upon fast cooling, atoms in the metal are prevented from forming a crystal when they arrange into icosahedra. Such arrangements are similar in appearance to fcc crystal structures but importantly cannot form large-scale, periodic structures (see image).

> "We have just reached the starting point to understand the true relationship between structure and properties of disordered materials."

To study the structure of metallic glasses, Chen, Akihiko Hirata and colleagues used an angstrom-beam electron diffraction technique in which a tiny beam of electrons is guided onto a sample of glass that is only a few atoms wide. As the electrons pass through the glass, they are reflected by the atoms and subsequently hit a screen that records the pattern of their reflection. With the help of computer analysis, the positions of the atoms in the sample can be determined from these patterns.

While the researchers were able to confirm the icosahedral atomic structure of metallic glasses, they also found that the icosahedra were not perfectly formed, as previously assumed. Interestingly, this slight distortion occurs in a way that makes the icosahedra appear even closer in structure to the fcc arrangement.

Beyond the discovery of local order in metallic glasses, the Angstrom-beam electron diffraction technique itself is a powerful way of studying compounds on the atomic scale, comments Chen. "We have just reached the starting point to understand the true relationship between structure and properties of disordered materials. We now have a reliable experimental method to directly investigate local atomic structure, and in the present case to show the correlation between atomic-scale structure and glass formation, and perhaps even the structural origin of the glass transition."

1. Hirata, A., Kang, L. J., Fujita, T., Klumov, B., Matsue, K., Kotani, M., Yavari, A. R. & Chen, M. W. Geometric frustration of icosahedron in metallic glasses. *Science* **341**, 376–379 (2013).

Published online on 26 August 2013

Batteries:

A crash course in nanofabrication

A collaborative study reveals that atomic collisions play critical roles during laser-driven assembly of electroactive thin films

A representation of the combined mathematical and materials study into the deposition of electroactive thin films. The simulated trajectory of a lithium atom at an oxygen pressure of 10^{-6} torr (black line) is superimposed over a plot of a lithium plasma plume after expanding for 5 microseconds at an oxygen pressure of 10^{-2} torr (background).

Developing high-capacity lithium ion batteries is an important research problem in materials science, and the realization of high-quality thin films of lithium metal oxides is a step toward this goal. Pulsed laser deposition (PLD) is a promising method of creating such films. In this technique, atoms from a lithium-containing source are vaporized using high-powered bursts of light, and the resulting 'plume' of plasma-phase atoms subsequently lands on a designated surface as a nanometer-thin coating.

However, when depositing films of electroactive materials such as lithium, the composition of the final thin film often differs from that anticipated. This 'non-stoichiometric' behavior makes it hard to predict the final result of particular fabrication strategies. Although the causes of the non-stoichiometry may be attributed to the volatile and chemically reactive nature of lithium atoms, quantitative explanations of this phenomenon have been lacking. Daniel Packwood, Susumu Shiraki and Taro Hitosugi from the AIMR at Tohoku University[1] have made a discovery that should significantly improve the quality of PLD lithium-based thin films thanks to a model that describes collisions between high-energy atoms during the deposition process.

> **"The team expects that their analysis can guide the fabrication of higher-quality interfaces that would lead to lithium ion batteries with higher charge–discharge rates by reducing the effects of electrical resistance."**

During experimental trials, the researchers noticed that adding background pressures of oxygen gas to the PLD chamber could change the proportion of lithium in the thin film structures. Intrigued by this result, they investigated this behavior — and the role of oxygen — with a theoretical model of the scattering process as a series of two-dimensional, head-on collisions between classical particles (see image).

After synthesizing several prototypical lithium–manganese oxide thin films at different oxygen pressures, Packwood, Shiraki and Hitosugi compared the films' chemical composition to the predictions of their new model. The results were striking: the theory correctly mirrored the experimental results and revealed that the presence of oxygen gas caused lithium ions to scatter in erratic trajectories, often violently. Heavier manganese atoms pushed through oxygen practically unimpeded. According to the team, these findings indicate that lighter atoms will always show deficiencies when background gas pressures rise above a certain threshold — thus, source materials must be chosen carefully to achieve desired lithium compositions.

Packwood notes that the model works well because it captures the physics behind the critical energy exchange occurring during atomic scattering. This ensures reasonable thermal equilibrium in the model and predictions of spatial distribution that have proven experimentally valid. The team expects that their analysis can guide the fabrication of higher-quality interfaces that would lead to lithium ion batteries with higher charge–discharge rates by reducing the effects of electrical resistance.

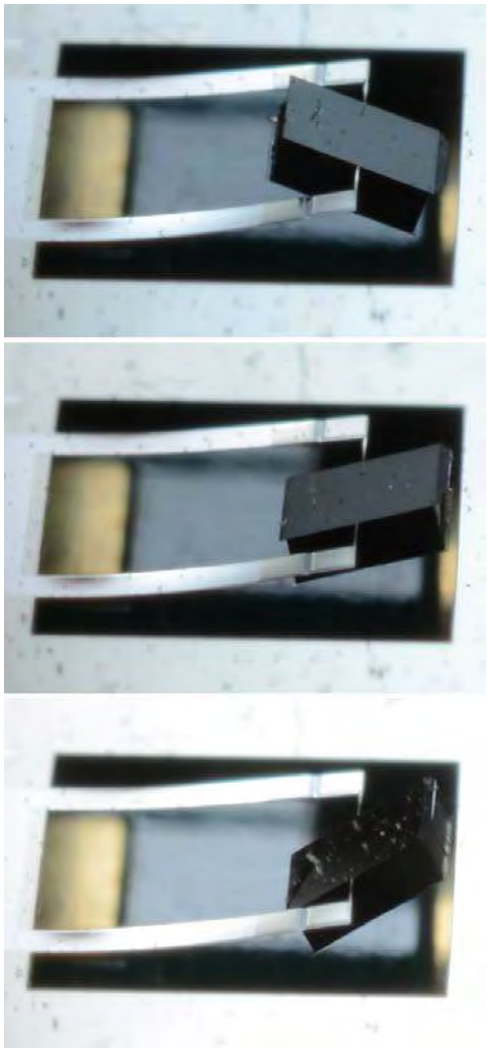
1. Packwood, D. M., Shiraki, S. & Hitosugi, T. Effects of atomic collisions on the stoichiometry of thin films prepared by pulsed laser deposition. *Physical Review Letters* **111,** 036101 (2013).

Metallic glasses:

'Revolutionary' advance in MEMS

Replacing silicon with a metallic glass enables a low-powered microelectromechanical system with a high rotational performance to be realized

The fragility of silicon after it has been subjected to microprocessing limits the use of silicon-based microelectromechanical systems, or 'MEMS', in devices with large rotational movements. Now, by exploiting the high robustness of metallic glasses, AIMR researchers have constructed a MEMS device that boasts an ultrahigh rotational performance as well as a very low power consumption, making it attractive for next-generation sensors and actuators[1].



The metallic-glass-based microscanner in action. Its metallic-glass components enable a much higher rotation angle to be achieved than that of a conventional silicon-based device.

Metallic glasses are alloys that are characterized by a non-crystalline structure and a low elastic modulus. Yu-Ching Lin first encountered them when she joined the AIMR at Tohoku University, and she was immediately struck by their potential for MEMS. "Metallic glasses are amorphous and are very strong on micro and nanoscales," she explains. "I thought they would be very promising for MEMS, which need tough micro and nanostructures to prevent breakage during actuation."

Lin realized that, because they have lower elastic moduli than silicon, metallic glasses could be used to realize a higher degree of movement in MEMS. This is exciting for sensing and actuating applications, since larger deflections mean higher performance.

To test this idea, Lin and her collaborators constructed a microscanner that contained a zirconium-based metallic glass (see image). The scanner had a large rotation angle of 146 degrees at a low power consumption in the microwatt range. Lin notes that it would be exceedingly difficult to realize such a large deflection angle and low power consumption simultaneously in a silicon-based MEMS.

To explore the potential of the scanner, the team deployed it as part of an optical coherence tomography imaging system, which they used to obtain images of a human finger. The metallic-glass MEMS scanner obtained images at a lateral resolution about ten times better than silicon-based scanners reported in the literature, says Lin. "Many MEMS researchers are developing microscanners for optical coherence tomography imaging based on silicon, with very slow scanning speeds."

Its high performance and enviably low power consumption make MEMS fabricated from metallic glasses promising for emerging wearable technology, for which fast-draining batteries are a concern. Looking further ahead, "if we can combine our device with a self-generation device, maybe in the future we won't even need a battery," says Lin.

Lin notes that both metallic glasses and MEMS are strong research fields at Tohoku University, and that working at the AIMR has enabled her and her collaborators to bridge the two fields and create this novel metallic-glass MEMS device.

1. Lin, Y.-C., Tsai, Y.-C., Ono, T., Liu, P., Esashi, M., Gessner, T. & Chen, M. Metallic glass as a mechanical material for microscanners. *Advanced Functional Materials* **25,** 5677–5682 (2015).

Three-way catalysts:

Cool way to make catalytic converters

Nanorods with high oxygen storing capacities at moderate temperatures have been synthesized using a simple reaction

A new, mild-temperature method for producing cerium oxide nanorods has been developed by AIMR researchers. The nanorods show an excellent oxygen storage capacity at temperatures below 200 degrees Celsius, making them promising for use as catalysts to control harmful emissions from vehicles[1].

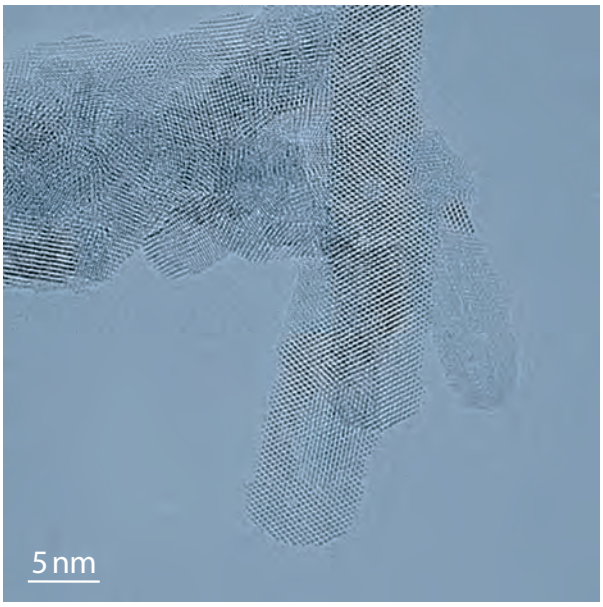
Catalytic converters in cars use so-called three-way catalysts to convert noxious pollutants such as carbon monoxide and nitrous oxides into more benign compounds. Cerium oxide is an attractive material for such catalysts due to its high oxygen storage capacity — a critical parameter for three-way catalysts.

However, most methods for fabricating nanostructures require high temperatures, which induce crystal growth and thereby have the detrimental effect of reducing the surface area of the nanostructures — another crucial parameter for catalysts. This has made it challenging to produce cerium oxide nanostructures that possess high oxygen storage capacities at temperatures below about 400 degrees Celsius.

Now, a team of five researchers from the AIMR at Tohoku University led by Naoki Asao and Koji Nakayama has devised a mild-temperature method for producing nanorods of cerium oxide that exhibit an excellent oxygen-storage capacity at moderate temperatures.

The nanorods are about 5 to 7 nanometers in diameter as measured by high-resolution transmission electron microscopy (see image). The cool reaction conditions made it possible to produce such fine structures.

The team adopted a method that they had previously developed to produce nanowires of sodium titanate. It basically involves corrosion of ribbons of cerium–aluminum alloys in an alkaline medium; in this reaction, aluminum is leached, whereas cerium is oxidized. Importantly, this reaction occurs under mild conditions.



A high-resolution transmission electron microscopy image showing fine cerium oxide nanorods fabricated by a mild-temperature method.

"This technique is really different from previous methods. Its key aspect is the mild fabrication conditions, which make it possible to fabricate fine structures," says Asao. "Based on our work with titanate nanowires, we had a feeling that the corrosion-based method would result in some unexpected properties. But the findings far exceeded our expectations."

Asao is very excited about the potential of this new method. "We believe that this research will have a significant impact on the automobile industry," he says. In addition, the researchers anticipate that the nanorods could be used in other applications, including fuels cells, ultraviolet blockers, solar cells and sensors.

By optimizing the reaction conditions and varying the composition of the cerium–aluminum mother alloys, the scientists will seek to further enhance the oxygen storage capacity and other properties of the nanorods to make them suitable for practical applications.

1. Ishikawa, Y., Takeda, M., Tsukimoto, S., Nakayama, K. S. & Asao, N. Cerium oxide nanorods with unprecedented low-temperature oxygen storage capacity. *Advanced Materials* **28,** 1467–1471 (2016).

Lithium–oxygen batteries:

Super-sized storage with nanoporous graphene

Unconventional electrodes made from three-dimensional graphene structures enable batteries to hold 100 times more charge than conventional lithium-ion cells

By converting flat graphene sheets into three-dimensional (3D) architectures, AIMR researchers have developed a lightweight, metal-free electrode for lithium–oxygen ($Li–O_2$) batteries that may have a transformative effect on all-electric vehicles[1].

The excess weight and moderate capacities of today's lithium-ion batteries have prompted a search for alternative technologies. Rechargeable lithium–oxygen batteries are a promising substitute because of their ultrahigh theoretical energy densities and ability to generate power by 'breathing' in oxygen from the atmosphere, negating the need for typical battery components.

These experimental batteries generally use a form of charcoal known as activated carbon as cathodes, and mix them with transition-metal catalysts. Activated carbon, however, becomes unstable under typical lithium–oxygen operating conditions — after several charge–discharge cycles, the carbon begins to decompose battery electrolytes, causing premature device failure.

Another approach is to use two-dimensional graphene lattices as lithium–oxygen cathodes because of their high surface area, good chemical and mechanical stability, and high electrical conductivity. But integrating graphene into electrochemical cells is problematic: graphene connects poorly with metal electrodes and catalysts and is geometrically difficult to pack into cells with sufficient density.

Mingwei Chen and Jiuhui Han of the AIMR and co-workers have recently developed a way to coax graphene out of its planar geometry by growing it on the nanoporous surfaces of disposable nickel templates. This produces 3D materials with abundant pore space for trapping molecules, and the same high-speed electron mobility as their flat counterparts. In their latest work, the researchers teamed up with colleague Tadafumi Adschiri to investigate 3D graphene as a potential electrode for lithium–oxygen batteries.

A nanoporous electrode made from graphene complexes can dramatically boost charge storage in 'breathable' lithium–oxygen batteries.

One advantage of nanoporous graphene is that bending the flat lattice into 3D shapes introduces defects that can host dopants — small guest atoms that alter the surface chemistry of the larger carbon framework. The team studied nitrogen- and sulfur-doped 3D graphene because these atoms can promote lithium–oxygen reactions without metal catalysts.

The researchers fabricated centimeter-scale, flexible graphene electrodes and placed them into 'coin-cell' type lithium–oxygen batteries (see image) that snap together without the need for complex assembly or binding agents. Electrochemical tests revealed the benefits of these electrodes — the nitrogen-doped nanoporous graphene had a discharge capacity two orders of magnitudes greater than that of commercial lithium batteries and could be reliably recharged for hundreds of cycles.

"These excellent performances surpass state-of-the-art metal-free, graphene-based lithium–oxygen batteries," says Han. "With such large capacities, they could transform portable electronics and power electric vehicles for extended ranges of more than 500 kilometers."

1. Han, J., Guo, X., Ito, Y., Liu, P., Hojo, D., Aida, T., Hirata, A., Fujita, T., Adschiri, T., Zhou, H. & Chen, M. Effect of chemical doping on cathodic performance of bicontinuous nanoporous graphene for Li-O_2 batteries. *Advanced Energy Materials* **6,** 1501870 (2016).

Band structure engineering:

Massless electrons put on weight

Massless electrons can be made massive by exploiting the spins in a layer of iron atoms on tungsten

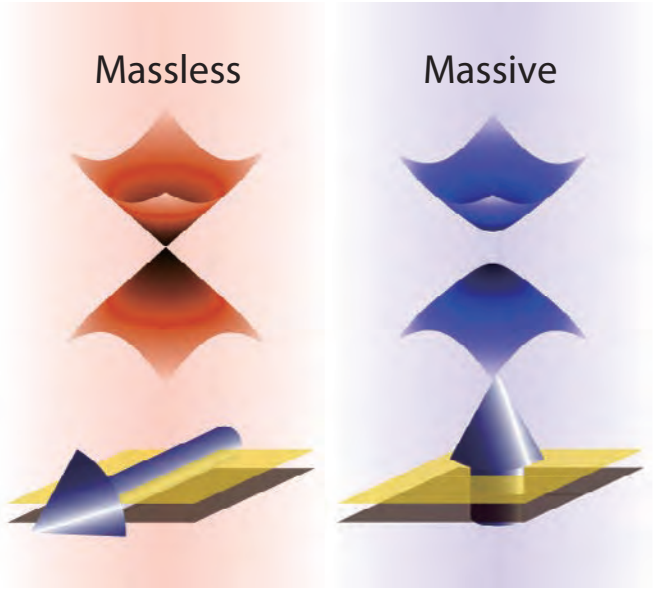
AIMR researchers have struck upon a convenient way to convert ultrafast electrons known as 'massless Dirac fermions' into ones that possess mass[1]. This has promise for realizing new devices such as magnetic-field sensors and magnetic memory devices.

Electrons moving through ultrathin layers on top of blocks of novel materials such as topological insulators have generated a lot of interest among materials scientists recently. Such electrons behave as essentially massless particles and move at speeds approaching that of light. Researchers strongly desire a way to manipulate Dirac fermions so that they can be easily changed between their massive and massless states.

Seigo Souma and co-workers at the AIMR, Tohoku University, have found a simple and effective way to convert massless Dirac fermions into massive ones: evaporate an atomically thin layer of iron atoms onto a small block of tungsten metal.

Unlike normal massive conduction electrons in metals, massless electrons lack a gap in their band structure. The ferromagnetism of the iron atoms opens a gap in the electrons' band structure, making the electrons massive. "This is the first spectroscopic observation of a gap opened by a magnetic effect for a system in which ferromagnetism has been confirmed," says Souma.

The researchers found that the electrons could be switched between massless and massive states by varying the direction of the spins of the iron atoms — the electrons are massless when the spins lie in the plane of the layer, but become massive when the spins are perpendicular to the layer (see image).



Electrons in an iron film (top yellow layer) on a tungsten substrate (bottom brown layer) are massless (no gap in the band structure) when the spins (indicated by purple arrows) of the iron atoms are in plane and massive (gap in the band structure) when the spins are perpendicular to the film.

The direction of the electron spins can be controlled by tuning the thickness of the iron film or adsorbing oxygen onto the film.

Their method has two advantages over alternative schemes. First, the iron layer exhibits strong ferromagnetism that should persist well above room temperature (roughly 300 kelvin). This is in contrast to systems doped with magnetic ions where ferromagnetism disappears above about 30 kelvin.

The second advantage is that the gap size is considerably larger than previous systems, being over twice that achieved in topological insulators doped with magnetic ions. Since this gap size is approaching the thermal energy at room temperature, it holds the promise of realizing devices that operate at room temperature.

The team is excited about applying the concept to other systems, particularly topological insulators. "Our idea is rather simple and should be applicable to other systems," notes Souma. "If we can find an appropriate overlay film that can be epitaxially grown on a topological insulator, various exotic phenomena will become experimentally accessible."

1. Honma, K., Sato, T., Souma, S., Sugawara, K., Tanaka, Y. & Takahashi, T. Switching of Dirac-fermion mass at the interface of ultrathin ferromagnet and Rashba metal. *Physical Review Letters* **115,** 266401 (2015).

Titanium dioxide:

Atoms mapped at border between crystals

Manipulating the structure of grain boundaries could fine-tune the properties of polycrystalline materials

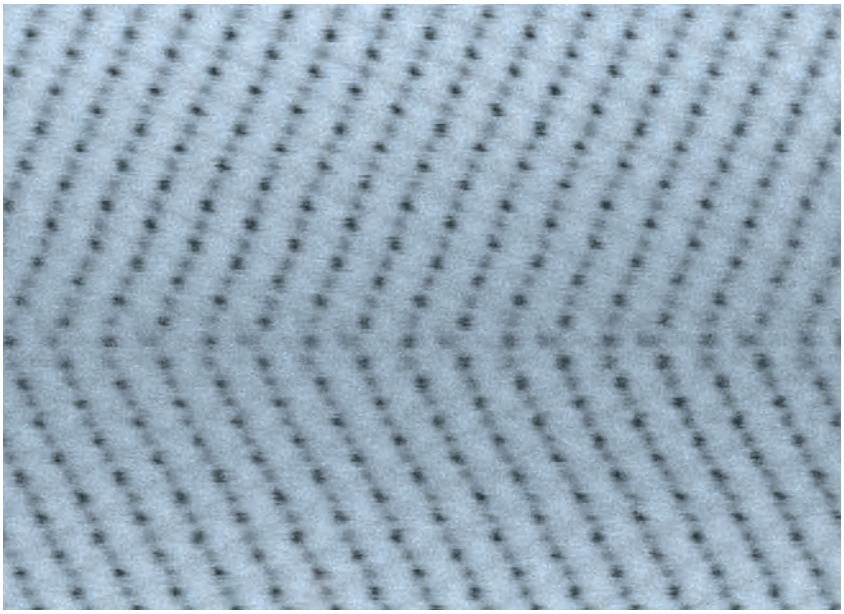
By pinpointing the precise positions of atoms in titanium dioxide, AIMR researchers have studied how temperature and pressure affect the materials' structure and properties[1].

As their name implies, polycrystalline materials are made up of many small crystals. The interfaces between two of these small crystals are known as grain boundaries, the structure of which strongly affects material properties such as strength and electrical conductivity. Temperature or pressure changes can cause defects in a crystal's atomic lattice to migrate to a grain boundary, which reshapes the structure of the boundary and hence modifies the material's properties.

This process is extremely difficult to study because researchers need to see exactly where atoms sit relative to a grain boundary. While scanning transmission electron microscopy (STEM) can offer some insights, its usefulness is limited if the material contains low-mass atoms such as oxygen, which scatter electrons only weakly and hence are difficult to image by conventional STEM.

Now, Yuichi Ikuhara of the AIMR at Tohoku University and co-workers have applied two advanced STEM techniques — aberration-corrected high-angle annular dark-field (HAADF) STEM and annular bright-field (ABF) STEM — to study titanium dioxide, which is used in a wide range of applications, including catalysis, solar cells and gas sensors. The position of oxygen atoms in titanium dioxide's grain boundaries can significantly affect the material's conductivity and catalytic activity.

To simulate a grain boundary, the researchers bonded two crystals of titanium dioxide together (see image) and used HAADF and ABF STEM to reveal a neat line of oxygen atoms along the boundary.



A scanning transmission electron micrograph showing a simulated grain boundary produced by combining two crystals of titanium dioxide.

When they heated these samples to 800 degrees Celsius under low pressure, the team found that some oxygen atoms were missing from the grain boundary. This should increase electrical conductivity along the boundary, says Ikuhara.

But heating the sample under a vacuum caused oxygen atoms to adopt a zigzag pattern along the grain boundary. "It is very surprising that these conditions could dramatically modify the atomic structure of grain boundaries in titanium dioxide," says Ikuhara. When the researchers performed theoretical calculations to simulate these changes, they obtained good agreement with the experimental observations.

The results suggest that the properties of polycrystalline materials could be fine-tuned through heat or low-pressure treatments, optimizing them for use in electronic devices, for example. "We could control the grain boundary atomic structures to convert an insulating grain boundary into a conductive one," suggests Ikuhara.

The team next plans to study how temperature and pressure affect the grain boundaries of other materials.

1. Sun, R., Wang, Z., Saito, M., Shibata, N. & Ikuhara, Y. Atomistic mechanisms of nonstoichiometry-induced twin boundary structural transformation in titanium dioxide. *Nature Communications* **6**, 7120 (2015).

Graphene:

Tying ribbons of graphene

Extremely thin ribbons of graphene grown on copper could open applications for the 'miracle material'

A method that produces tiny units of graphene and joins them together to form highly connected stripes has been found by AIMR researchers. This 'bottom-up' fabrication technique could unleash graphene's potential for use in high-speed, low-power electronic devices.

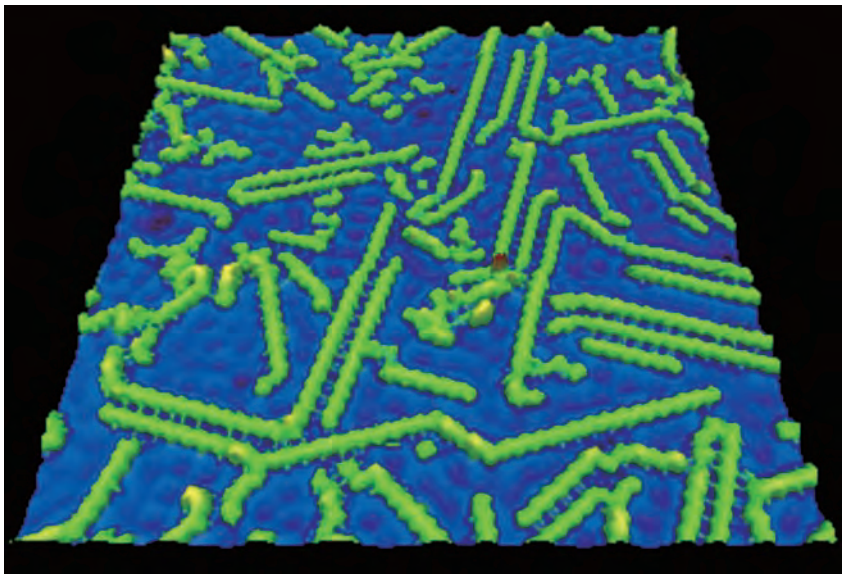
Since its discovery in 2004, graphene has generated much excitement due to its remarkable electronic and mechanical properties. But for it to become useful in applications, scientists need a way to combine graphene nanostructures such that they form macroscale components while still preserving graphene's excellent properties.

Extremely narrow (thinner than 50 nanometers) stripes of graphene, known as graphene nanoribbons, promise to achieve this, but current processing methods produce either well-connected nanoribbons that contain defects or entangled bundles of nanoribbons that are defect free.

Now, Patrick Han of the AIMR at Tohoku University and his co-workers have found a way to produce well-connected strings of nanoribbons without defects[1]. Their method produces good-quality graphene nanoribbons and connects their ends so that they form chemically and electronically connected structures (see image).

The researchers found that, on applying heat, a copper substrate guides precursor molecules to form and connect graphene ribbons. The lengths and growth directions of the nanoribbons could be controlled by varying the substrate properties and the temperature.

"There are two outstanding questions regarding how graphene can be applied in electronics," comments Han. "One is how to fabricate atomically precise graphene structures with high aspect ratios at desired locations, while the other is how to make electronic connections between these structures to access graphene's properties."



A topographic scanning tunneling microscopy image showing graphene nanoribbons (green) grown on a copper substrate (blue).

The method provides answers to both questions. "If precursor molecules are allowed enough time and space to align, graphene nanoribbons with very high aspect ratios can be produced without defects. Moreover, graphene nanoribbon interconnections yield smooth electronic connections, showing that bottom-up strategies can access graphene's amazing properties."

Han notes that while other two-dimensional materials have recently been stealing the spotlight from graphene, it still has a unique advantage — organic chemistry can be used to fabricate defect-free structures from designer precursors. "In this regard, our method is a significant advance — the use of bottom-up graphene fabrication strategies may lead not only to the production of future graphene nanodevices, but also to the integration of non-graphitic materials."

Since copper substrates limit growth to six directions, growing graphene nanoribbons inevitably collide, limiting their length. The team intends to overcome this restriction by finding strategies to limit growth to a single direction.

1. Han, P., Akagi, K., Federici Canova, F., Shimizu, R., Oguchi, H., Shiraki, S., Weiss, P. S., Asao, N. & Hitosugi, T. Self-assembly strategy for fabricating connected graphene nanoribbons. *ACS Nano* **9,** 12035–12044 (2015).

Gold catalysis:

Examining catalysis on an atomic scale

A comparison of atomic maps of nanoporous gold and catalysis reveals that surface defects are important catalysis sites

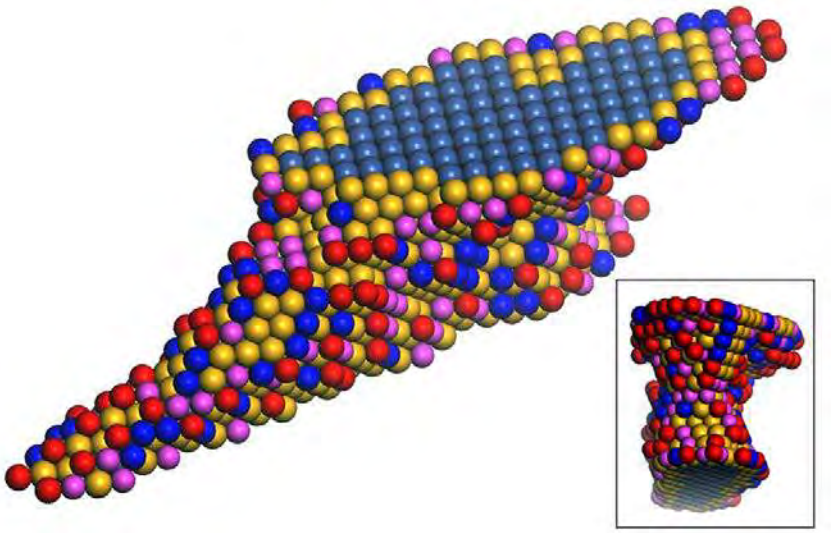
By mapping the three-dimensional arrangement of gold atoms in gold structures containing nanoscale pores, researchers at AIMR have shown that surface defects play an important role in their catalytic ability[1].

Gold nanostructures are widely used to accelerate oxidation reactions. For example, they can catalyze the oxidation of toxic carbon monoxide to benign carbon dioxide. But just how they speed up these reactions has been vigorously debated for many years.

One complicating factor is that gold nanoparticles are often supported on oxide surfaces, which makes it difficult to determine the degree to which substrate effects contribute to catalysis. Ideal systems for studying gold's intrinsic catalysis are gold structures riddled with tiny pores — nanoporous gold — because, unlike nanoparticles, they do not need to be attached to a substrate.

Now, Mingwei Chen and Pan Liu of the AIMR at Tohoku University and co-workers have combined a state-of-the-art electron microscopy technique with tomography to visualize in three dimensions the atomic arrangements of narrow bridges in nanoporous gold (see image). They then compared these three-dimensional maps with measurements of catalysis.

In addition to showing the positions of atoms, the images also reveal their degree of coordination to surrounding atoms. Atoms far from a surface are completely surrounded by atoms and hence have high coordination numbers, whereas those near or on a surface have lower ones. The researchers found qualitative agreement between the electron microscopy characterization and catalytic measurements at active atomic sites and low-coordinated surface atoms. This implies that defects on the surface play a major role in the catalysis of nanoporous gold.



The atomic positions of a narrow bridge in nanoporous gold. The colors indicate the coordination numbers (red: five or six; blue: seven; pink: eight; yellow: nine to eleven). The inset shows the same structure from a different perspective.

"The curved surface of nanoporous gold is composed of flat terraces, atomic steps and kinks, which correspond to different coordination numbers," explains Liu. "Generally, under-coordinated sites with low coordination numbers of five and six are thought to be highly active sites in oxidation reactions, whereas those with coordination numbers greater than nine are considered to be relatively inactive. Our study has confirmed this and provides compelling evidence that catalysis may originate from the under-coordinated surface atoms alone."

Liu notes that the method could also be applied to other catalytic systems. "This study also demonstrates that quantitative measurements on an atomic scale can provide vital knowledge about the catalytic mechanisms of nanomaterials."

In the future, the team intends to improve the catalytic performance of gold catalysts by fabricating and measuring the catalytic properties of nanoporous gold particles with larger surface areas and more under-coordinated atoms.

1. Liu, P., Guan, P., Hirata, A., Zhang, L., Chen, L., Wen, Y., Ding, Y., Fujita, T., Erlebacher, J. & Chen, M. Visualizing under-coordinated surface atoms on 3D nanoporous gold catalysts. *Advanced Materials* **28,** 1753–1759 (2016).

Graphene:

A dose of calcium yields a superconductor

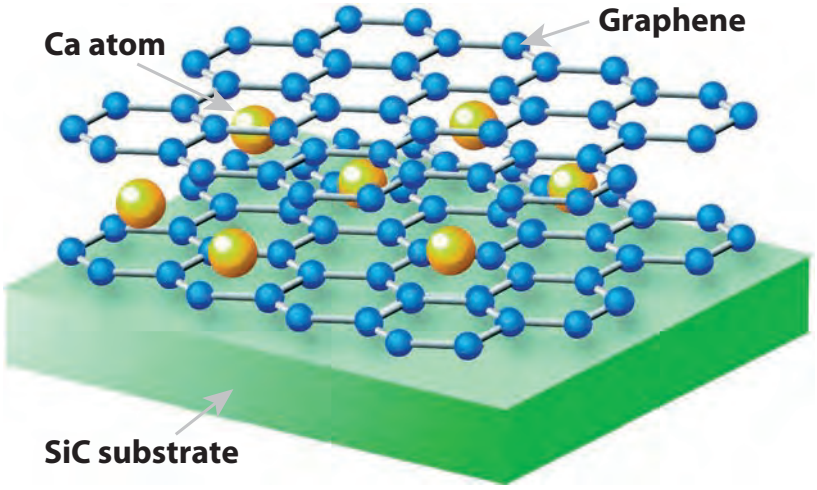
Sandwiching calcium atoms between two layers of graphene produces a device that moves electrons with zero resistance

The first direct evidence of graphene acting as a superconductor has been reported by AIMR researchers[1]. This demonstration, which occurs at temperatures close to absolute zero, sets the stage for molecular-scale devices that can move electrons effortlessly and do not generate waste heat.

Ever since layers of graphene — one-atom-thick sheets of carbon atoms — were first isolated, researchers have been fascinated with the way electrons behave as near-massless particles when they move between its carbon atoms. This remarkable electron mobility has raised the exciting possibility of producing superconducting graphene, but unfortunately graphene has too few electrons to realize zero-resistance flow.

Now, Takashi Takahashi and colleagues from the AIMR at Tohoku University and the University of Tokyo have developed a method that boosts the electron density of graphene to the requisite levels for superconductivity. They grew two layers of graphene on top of silicon carbide and then sandwiched calcium atoms between the two graphene sheets to improve the material's conductivity.

"Fabricating genuine bilayer graphene is challenging because other products, such as single- and tri-layer graphene, can form, and they complicate data analysis," says Takahashi. To overcome this problem, the researchers performed their experiments in extremely clean, ultrahigh-vacuum environments and monitored graphene growth as it occurred. They found that optimizing the precise timing of temperature changes was critical for controlling the number of graphene layers.



'Bilayer' graphene, controllably grown from a silicon carbide (SiC) substrate, becomes superconductive when infused with calcium (Ca) atoms.

Finding the best way to insert calcium into the bilayer graphene was just as vexing. Simple deposition techniques were unsuccessful, probably because calcium atoms are too large to squeeze into the sandwich. "Instead, we developed a special 'atom-replacement' method," notes Takahashi. In this technique, smaller lithium atoms are deposited into bilayer graphene, thereby expanding the interlayer distance. Calcium atoms are then placed on top of the graphene, and they swap places with the sandwiched lithium atoms on heating (see image).

The researchers used a custom-made four-point probe to measure the calcium–graphene material inside the ultrahigh-vacuum chamber. When they gradually lowered the temperature to 4 kelvin, they saw the much-desired zero-resistance state. In contrast, pure bilayer graphene and the lithium-doped material showed no signs of superconductivity.

"We were all excited when we saw these experimental results," says Takahashi. "They indicate that superconductivity is driven by charge transfer from the calcium atoms to the graphene sheets."

The team is currently exploring using different graphene layer structures and metal atoms to raise the onset of superconductivity to more practical temperatures.

1. Ichinokura, S., Sugawara, K., Takayama, A., Takahashi, T. & Hasegawa, S. Superconducting calcium-intercalated bilayer graphene. *ACS Nano* **10,** 2761–2765 (2016).

Photonics:

Multitasking molecule simplifies organic LED design

Ring-shaped organic molecules simplify the design of organic light-emitting diodes, without sacrificing efficiency

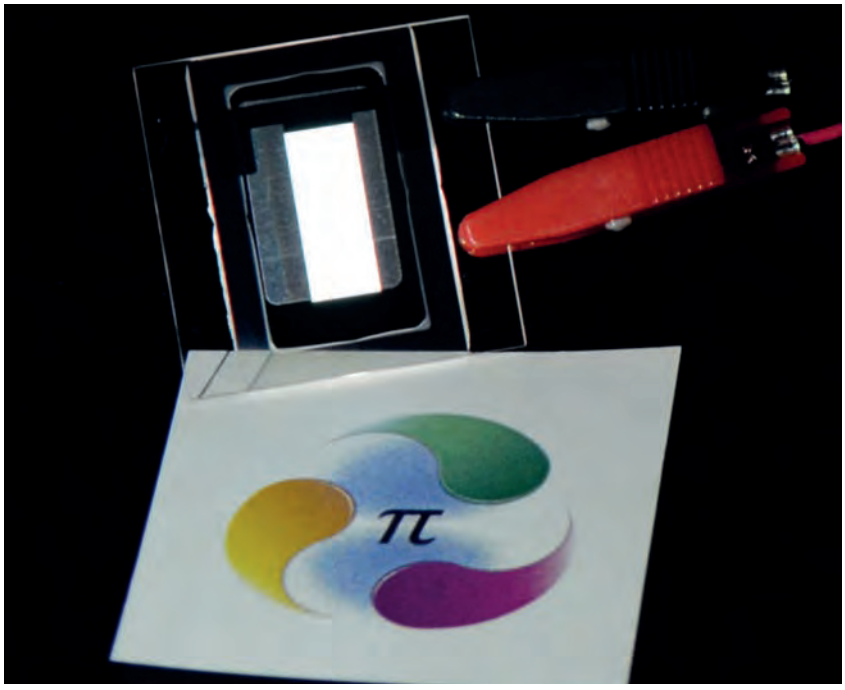
A ring-shaped molecule can play multiple roles in an organic light-emitting diode (OLED)[1]. This finding by AIMR researchers could simplify the manufacture of these devices without reducing their performance.

OLEDs contain a layer of carbon-based molecules that emit light when an electric current passes through them. They have many advantages, including being thin, light and potentially flexible, as well as consuming relatively little energy. They are thus being increasingly used in electronic devices like mobile phones and displays.

Many OLEDs contain multiple layers of different materials, each of which performs a specific function. For example, one layer carries negative electrons, while another transports positive holes — the gaps left by missing electrons. When electrons and holes meet, they bind to produce a high-energy 'exciton' state. Some OLEDs use a phosphorescent material that converts excitons into light; this requires yet another layer to prevent electrons or holes escaping from the phosphorescent emitter.

Hiroyuki Isobe of the AIMR at Tohoku University and co-workers have studied a family of molecules that can perform most of these tasks in a single layer, potentially allowing for much easier fabrication of OLEDs. These molecules, known as cyclo-*meta*-phenylenes (CMPs), are based on a large ring consisting of five or six benzene molecules.

The team tested these ring-shaped molecules in combination with a common phosphorescent emitter. Several of them were "completely useless", says Isobe. But one of them, a ring of five substituted benzenes called 5Me-[5]CMP, far exceeded expectations.



This white-light organic light-emitting diode contains a single layer of multitasking ring-shaped molecules.

It could transport electrons and holes, provide a place for them to form excitons and pass excitons on to the phosphorescent emitter. Crucially, it also slowed holes down so they could not escape, ensuring their complete conversion to light. Consequently, this OLED had an external quantum efficiency of up to about 23 per cent — almost as good as the best single-layer OLED and comparable with those of multilayer OLEDs. One reason for this high efficiency is that the 5Me-[5]CMP is a flexible molecule that can get very close to the iridium-based emitter to pass on excitons.

The team then blended 5Me-[5]CMP with red, blue and green emitters to make a white-light OLED, which had an efficiency of about 10 per cent (see image). "This is still a very premature demonstration, because the device architecture was not optimized," notes Isobe.

The team is improving the chemical synthesis of the CMPs to create molecules that reach even higher device efficiencies. Isobe adds: "AIMR is an ideal place for such interdisciplinary investigations."

1. Xue, J. Y., Izumi, T., Yoshii, A., Ikemoto, K., Koretsune, T., Akashi, R., Arita, R., Taka, H., Kita, H., Sato, S. *et al.* Aromatic hydrocarbon macrocycles for highly efficient organic light-emitting devices with single-layer architectures. *Chemical Science* **7,** 896–904 (2016).

Silicon monoxide:
Atomic structure revealed at last

A powerful new diffraction technique exposes the atomic structure of amorphous silicon monoxide, a promising electrode material for lithium-ion batteries

AIMR researchers have used state-of-the-art experimental techniques and calculations to definitively determine the atomic structure of amorphous silicon monoxide (SiO) for the first time[1].

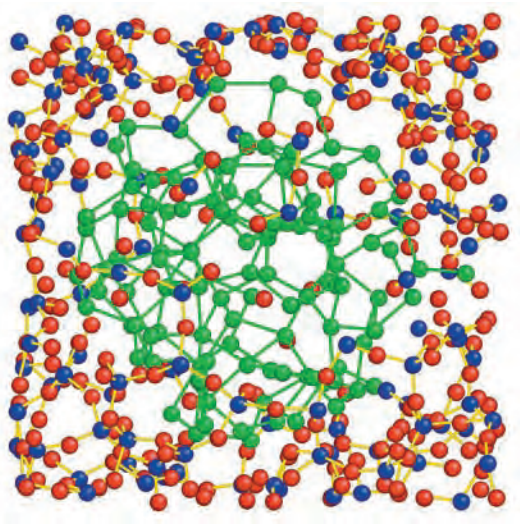
Lithium-ion batteries power everything from mobile devices to electric vehicles, yet the race to improve their capacity continues. Silicon-based anodes are promising in this pursuit, because silicon can hold more lithium than common carbon-based materials. However, the structure of crystalline silicon deteriorates over charging cycles, reducing cell performance. In contrast, amorphous (non-crystalline) silicon monoxide does not suffer from such deterioration.

But despite having been extensively researched for nearly a century, the atomic structure of amorphous silicon monoxide had not been fully determined, making it difficult to exploit the material's full potential.

"Amorphous silicon monoxide is a promising electrode material for lithium-ion batteries," says Akihiko Hirata of the AIMR at Tohoku University. "But to understand its charge–discharge mechanism at the atomic level, it is vital to know the details of its atomic structure."

Hirata, Mingwei Chen and co-workers, along with collaborators at the National Institute for Materials Science (NIMS) and Nissan, have succeeded in determining the atomic structure of silicon monoxide by using an array of impressive experimental techniques and calculations.

They used angstrom-beam electron diffraction, a technique that Hirata and Chen had previously developed, to obtain diffraction data from nanoscale regions of the material. In combination with synchrotron X-ray scattering and computer simulation results, their investigation revealed that on an atomic scale, silicon monoxide consists of a mixture of clusters of silicon and silicon dioxide with 'suboxide' regions in between (see image).



Atomic structure of amorphous silicon monoxide. The green spheres represent silicon atoms that form part of a silicon cluster, while the red and blue spheres respectively indicate silicon and oxygen atoms that make up a silicon dioxide matrix.

There had been much debate about the atomic structure of amorphous silicon monoxide. Previous studies had suggested that it consisted of an equilibrium mixture of amorphous silicon and silicon dioxide, but this model could not explain X-ray diffraction patterns. Conventional experimental techniques lack the spatial resolution to discover the atomic-scale structure, but angstrom-beam electron diffraction overcomes this restriction using an electron beam smaller than 1 nanometer in diameter.

The team is excited about the potential of their method for determining local atomic structures in amorphous materials. "Heterogeneous amorphous materials such as silicon monoxide are important for next-generation energy devices," says Hirata. "Our method will enable more-reliable models to be obtained. It promises to be a powerful tool for understanding their atomic structures as well as for providing valuable information about their functions."

The team intends to use their technique to analyze other amorphous oxides for batteries and chalcogenides for phase-change memory devices.

1. Hirata, A., Kohara, S., Asada, T., Arao, M., Yogi, C., Imai, H., Tan, Y., Fujita, T. & Chen, M. Atomic-scale disproportionation in amorphous silicon monoxide. *Nature Communications* **7,** 11591 (2016).

Lithium-ion batteries:

Nanocarbon electrodes are true lifesavers

Doughnut-shaped materials are key to the design of safer rechargeable batteries with impressive storage capacities

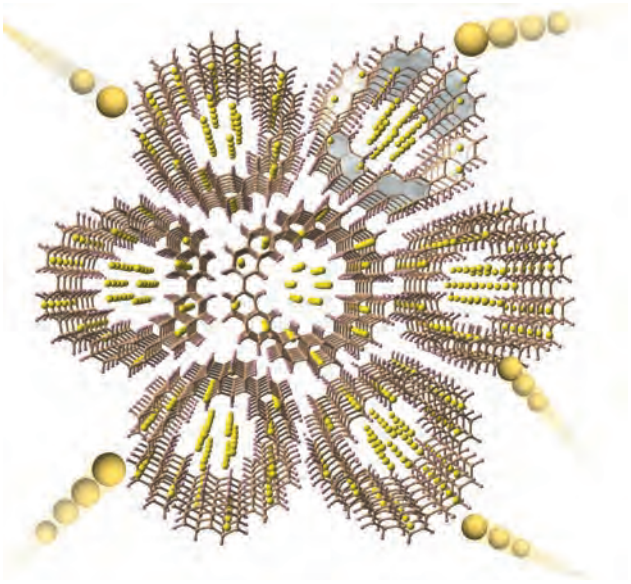
A material that packs high levels of lithium ions into well-ordered nanochannels can open the door to all-solid-state batteries, reports a joint team from the AIMR[1].

Rechargeable batteries, such as those used to power mobile phones, employ graphite as negative electrodes to store and release lithium ions. To meet consumer demand for longer-lived batteries, researchers are exploring different, nanostructured electrodes. In addition, the emergence of solid-state electrolytes, which are safer than conventional liquid electrolytes, is further driving the search for novel electrodes.

Now, Hiroyuki Isobe, Sota Sato and Shin-ichi Orimo from the AIMR at Tohoku University and colleagues have developed a nanostructured substance that can reversibly store and supply more lithium ions than conventional graphite electrodes. The team's compound, known as [6]cyclo-2,7-napthylene (CNAP), is a flat, aromatic molecule. It is based on ultrathin graphene molecules but with a critical difference — it has an empty, central opening that spans almost a nanometer.

The Isobe group originally designed CNAP as a material for organic light-emitting diodes. They demonstrated bipolar charge transport with this compound but did not find any unique effects arising from its hole-like defect. Instead, through collaboration with the Orimo group, the team explored whether CNAP's pore could be used for lithium-ion electrodes.

The researchers fabricated a solid-state battery by milling and then pressing a mixture of CNAP and the crystalline electrolyte lithium borohydride ($LiBH_4$) together into a pellet. Supplying the composite with a lithium foil completed the cell and enabled the battery's capabilities to be examined. The team saw a dramatic increase in lithium storage — nearly double the levels in graphite electrodes — that remained high even after multiple charge–discharge cycles.



A porous, graphene-like compound that forms ordered nanochannels in the crystal state can hold high amounts of lithium ions (yellow spheres) to realize longer-lasting batteries.

Figure courtesy of Takuji Ikeda, National Institute of Advanced Industrial Science and Technology (AIST)

Synchrotron X-ray analysis revealed that the doughnut-shaped CNAP stacked side-by-side to produce extended networks of one-dimensional, nanoscale pores (see image); nearly 10 per cent of the electrode contained empty space to hold excess charge. Quantum mechanical models showed that this process is energetically favorable, with each CNAP able to capture up to 18 lithium ions.

Discovering that CNAP was compatible with solid-state electrolytes was a pleasing surprise for Sato and Isobe. "Naphthalene and $LiBH_4$ are ubiquitous reagents that appear in any basic textbook for organic chemists," they note. "But according to received wisdom, they are not expected to react together. This 'no-reaction relation' of our composite electrode was key to its quick, reversible operation."

The team is currently exploring the design of functional pores by synthesizing new additions to their library of hydrocarbon-based cyclic molecules.

1. Sato, S., Unemoto, A., Ikeda, T., Orimo, S. & Isobe, H. Carbon-rich active materials with macrocyclic nanochannels for high-capacity negative electrodes in all-solid-state lithium rechargeable batteries. *Small* **12,** 3381–3387 (2016).

Metallic glasses:

Spotting secret relaxations

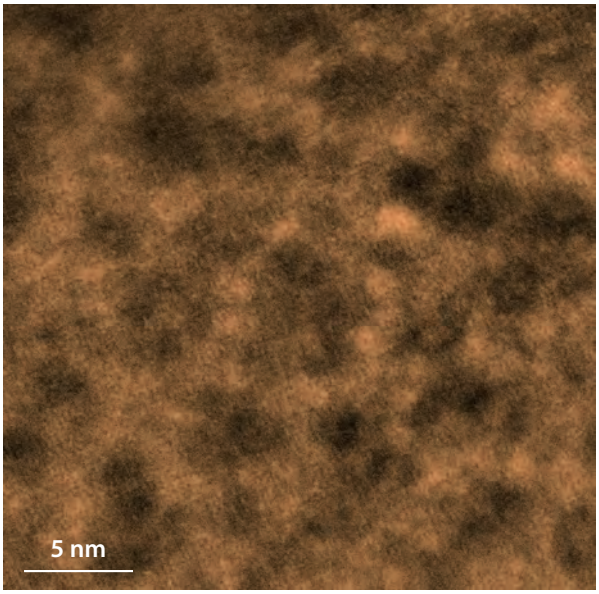
Direct evidence for structural changes that occur during metallic glass relaxation should facilitate the commercialization of super-tough alloys

Despite being stronger than steel, metallic glass alloys suffer from a heating-induced brittleness that limits their use in practical applications. A team from the AIMR has now used dynamic microscopy techniques to shed light on nanoscale structures that play key roles in determining the properties of metallic glasses[1].

Metallic glasses are made by supercooling molten metal atoms, such as zirconium, aluminum and copper, so that they form tightly packed solids with random molecular structures instead of regular crystals. When the atoms are taken out of their high-energy state, they mechanically relax through two processes: α- and β-relaxations. Primary α-relaxations disappear as the mixture is cooled below its glass transition temperature, whereas secondary β-relaxations keep occurring well after the alloy has been cast — these atom movements can lead to 'aging effects' as well as permanent plastic deformation.

Despite their importance, β-relaxations are only partially understood. Theoretical models indicate that spatial non-uniformity in the glass is responsible for aging effects, but corroborating experimental evidence had been missing. "It's a dynamic process, so the key obstacle is designing a characterization experiment that can catch such a time-dependent phenomenon," says Fan Zhu from the AIMR at Tohoku University.

Zhu, Mingwei Chen and their colleagues developed a technique to tune the degree of β-relaxations in a metallic glass by heating at temperatures below the glass transition point for varying lengths of time. They then characterized the samples using amplitude-modulation atomic force microscopy (AM-AFM) and scanning transmission electron microscopy (STEM) to see any disruption of nanoscale structures.



A scanning transmission electron microscopy image of a metallic glass shows that the structure contains cluster regions (dark areas in the micrograph) where atoms can still move after cooling to room temperature.

While most AFM experiments use a tiny vibrating cantilever to trace the height of surface atoms, AM-AFM measures variations in the amplitude and phase of the oscillating tip. These dynamic tip movements, explains Zhu, are very useful for measuring how metallic glasses behave both as elastic solids that snap back into shape after being twisted and as viscoplastic materials whose atoms can permanently flow into new locations.

By comparing the structural characteristics of relaxed metallic glasses with those of a hypercooled metallic glass, the team found that atomic movements were confined to small, isolated regions during β-relaxation. These regions were clear enough to resolve in STEM images as contrasting dark and bright regions, just a few nanometers in diameter (see image).

Zhu notes that this establishment of a definite link between β-relaxations and nanoscale inhomogeneous zones can aid researchers to exploit the unique properties of amorphous materials. "With this structural scheme, we can fill in the knowledge gaps between the properties and models of glasses," he adds.

1. Zhu, F., Nguyen, H. K., Song, S. X., Daisman, P. B. A., Hirata, A., Wang, H., Nakajima, K. & Chen, M. W. Intrinsic correlation between β-relaxation and spatial heterogeneity in a metallic glass. *Nature Communications* **7**, 11516 (2016).

Spintronics:

A clean look at magnetic semiconductors

Probing high-quality crystals with ultraviolet light reveals how spin-polarized electrons might power future low-energy memory devices

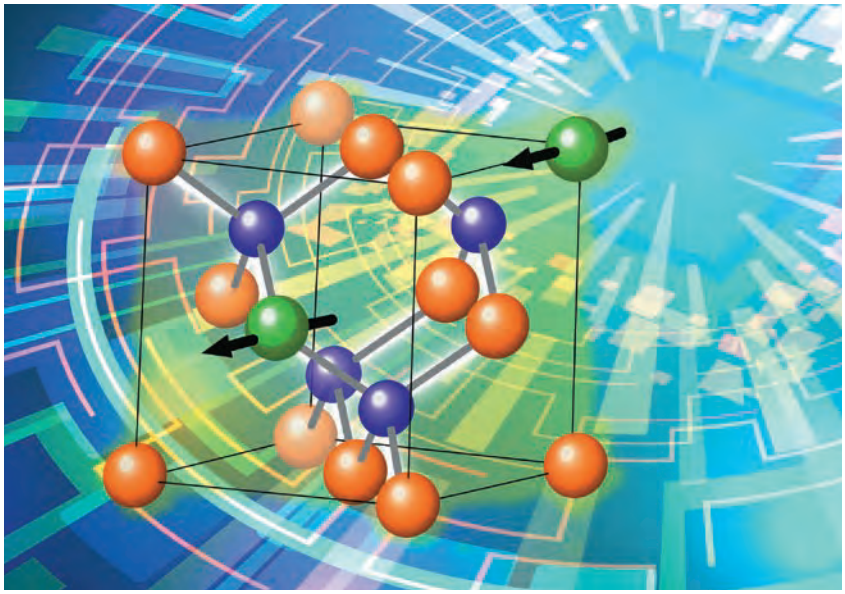
An improved way to prepare ultraclean magnetic semiconductor surfaces that includes using a special 'vacuum suitcase' to move samples has helped AIMR researchers crack a two-decade-old puzzle regarding active charge carriers in these promising spintronic materials[1].

Semiconductors made from gallium arsenide (GaAs) can exhibit intriguing properties when small amounts of manganese (Mn) atoms are incorporated into their structure. This is because the manganese dopants add permanent magnetic fields and positive-charge carriers to the semiconductor, allowing currents to be polarized into either up or down quantum spin states.

These characteristics have enabled researchers to use GaMnAs as a platform for new devices, such as spin transistors and magnetic memory, which can process information using minimal energy. However, understanding the carrier-induced magnetic properties of this semiconductor is tricky because effects from randomly distributed dopants are difficult to predict using standard quantum theory.

To settle this scientific debate, Seigo Souma of the AIMR at Tohoku University and his co-workers used a technique known as angle-resolved photoemission spectroscopy (ARPES) to directly probe the electronic band structure of GaMnAs and measure the 'Fermi level' at which dopant carriers are active.

In these ARPES measurements, high-intensity ultraviolet light stimulated crystals to emit electrons, which were analyzed to map out the relation between a charge carrier's wave-like momentum and its energy. "This is the only way to determine the Fermi-level position of GaMnAs," says Souma. "However, there are major problems inherent with its surface."



High-powered photon sources have been used to determine how magnetic dopant atoms (green spheres) can enable control over spin currents in semiconductor devices.

Souma explains that since ARPES probes the upper few nanometers of a millimeter-sized scan area, it needs extremely clean and reliable surfaces. Unfortunately, merely exposing GaMnAs to air causes thick oxides to grow, which obscure the electron signal. The team overcame this problem by developing a suitcase capable of maintaining a vacuum nearly as devoid of atoms as outer space. They then used the suitcase to transport high-quality samples from a growth chamber to the ARPES system.

The ARPES results revealed that the Fermi level of GaMnAs lies deep within the electron-rich, or valence, band of the semiconductor — a location that helped the researchers select an appropriate theoretical model to describe the carrier-induced ferromagnetism.

Intriguingly, their measurements also showed that the intensity of emitted electrons depended on the orientation of an applied magnetic field, an effect known as magnetic linear dichroism. "Observing this effect with ARPES indicates strong spin–orbit coupling in our sample," says Souma. "This is the main parameter needed to realize electric control over spin for computing and memory devices."

1. Souma, S., Chen, L., Oszwałdowski, R., Sato, T., Matsukura, F., Dietl, T., Ohno, H. & Takahashi, T. Fermi level position, Coulomb gap, and Dresselhaus splitting in (Ga,Mn)As. *Scientific Reports* **6,** 27266 (2016).

Three-dimensional graphene:

Sponge-like nanomaterials soak up electrons

Nanoporous graphene becomes an ultra-responsive transistor when filled with ionic liquids

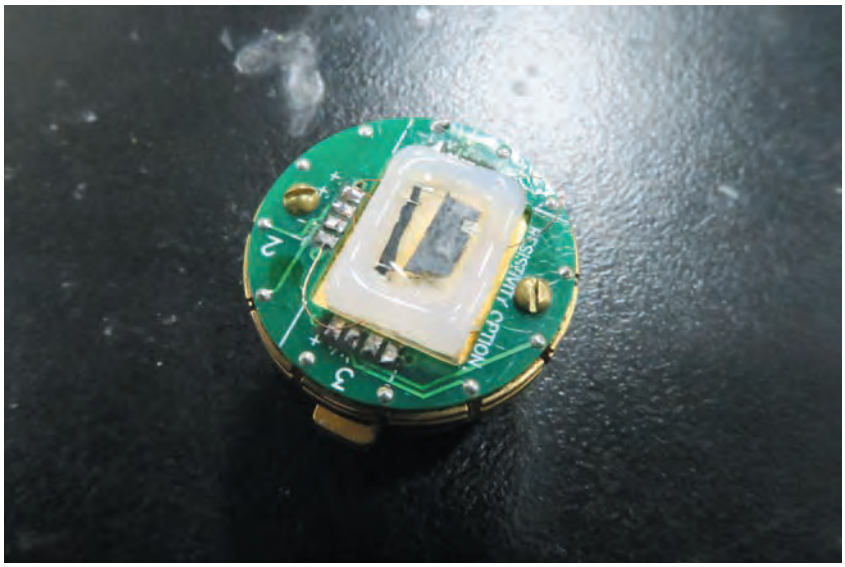
Using their expertise for growing highly crystalline, three-dimensional (3D) graphene structures, AIMR researchers have produced a transistor with 1,000 times greater capacitance and conductance than transistors made from flat films of graphene[1].

Electrons in graphene films have extraordinary mobility because they behave as particles with practically zero mass — so-called Dirac fermions. But graphene's flat structure limits the number of electrons it can hold, making it challenging to incorporate graphene films in devices such as transistors.

One way to boost the capacitance of graphene-based devices is to assemble graphene films into porous nanoarchitectures that have large surface areas. However, it is tricky to preserve the high electron mobility of graphene in such 3D graphene 'sponges' because most fabrication methods introduce many defects, which retard or scatter charges.

Mingwei Chen from the AIMR at Tohoku University and colleagues recently developed a technique that overcomes this problem using nanoporous nickel templates. These hard metal surfaces enable the growth of 'bicontinuous' 3D graphene structures that bend and bond smoothly with few structural gaps.

In their latest work, the AIMR team shows how to transform their 3D graphene structures into an electric double-layer transistor (EDLT) (see image). Unlike most transistors, the gates that control electron flow in EDLTs are made from nanometer-thin, capacitor-like charge layers that form at interfaces between an ionic liquid and a solid. The remarkably high accumulation of charges in the EDLT enables the electronic states of graphene to be controlled at very low operating voltages.



Photograph of an electric double-layer transistor (EDLT) based on three-dimensional, nanoporous graphene structures. Its capacitance and conductance are 1,000 times greater than those made from flat graphene films.

"This is one of the key devices needed to realize device applications with nanoporous graphene," explains Yoichi Tanabe, a co-author of the study. "It allows us to control the number of carriers in the bicontinuous nanoporous material through the electric-field effect."

After drying their 3D graphene structures under supercritical conditions to avoid damaging them, the researchers infused them with ionic liquid electrolytes and assembled the components into an EDLT. Using electrical measurements under a magnetic field, they developed a way to evaluate the nanoporous material's mobility. They discovered that the advantageous properties of Dirac fermions remained. The device also offered exceptional electron switching behavior and conductance for further transistor applications.

"Being able to tune carrier densities means our nanoporous graphene EDLT can be a basis to design other electric devices. For example, high-response photodetectors could be developed in the future," says Tanabe. "Also, diminishing the pore size in nanoporous graphene can introduce energy gaps into its electronic structure. Our EDLT technique could be one way to access these electronic states."

1. Tanabe, Y., Ito, Y., Sugawara, K., Hojo, D., Koshino, M., Fujita, T., Aida, T., Xu, X., Huynh, K. K., Shimotani, H. *et al.* Electric properties of Dirac fermions captured into 3D nanoporous graphene networks. *Advanced Materials* **28,** 10304–10310 (2016).

Electrocatalysis:

Splitting water without breaking the bank

Exploiting the alloying effect offers a cheaper way to produce clean hydrogen fuel from water

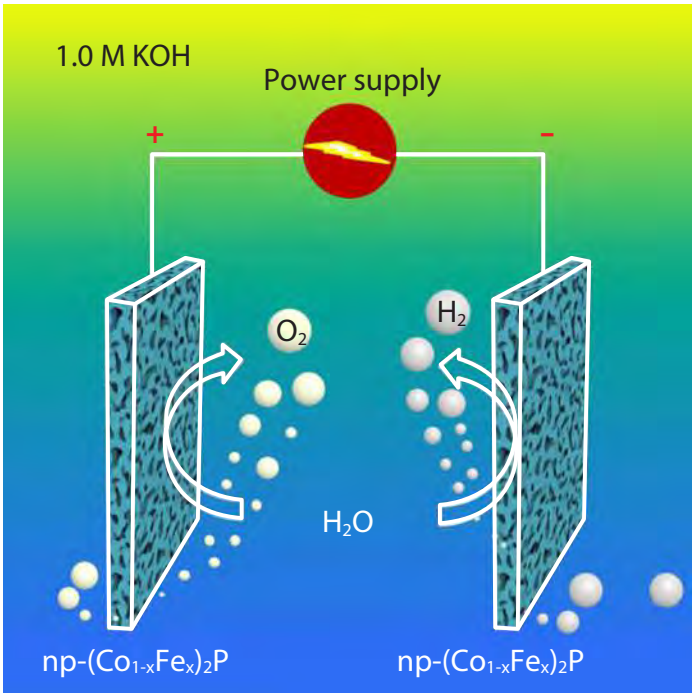
An inexpensive catalyst formed from two common metals could offer a new way to produce fuel from water, AIMR researchers have shown[1].

'Water splitting' is an electrochemical process in which water molecules are broken apart to release hydrogen — a useful fuel. The process is a promising way to store renewably generated electricity since stored hydrogen can be used to generate electricity at times when the Sun is obscured by clouds or there is no wind. However, most electrochemical catalysts for efficiently splitting water contain rare precious metals, such as platinum, making them prohibitively expensive.

Now, by exploiting a phenomenon known as the alloying effect, Yongwen Tan from the AIMR at Tohoku University and his colleagues have developed an inexpensive alternative. Their electrocatalyst is a material called a nanoporous phosphide and contains the common metals iron and cobalt. Tan says it rivals the performances of commercial water-splitting systems based on platinum.

Alloys are materials in which one element is added to enhance the properties of another. For example, adding tin to copper creates the alloy bronze, which is stronger than copper. But alloying does not just enhance the strength of materials. "Alloying has long been known to be an effective method to create new functions of catalytic materials," says Tan.

Tan's team anticipated that adding iron to cobalt phosphide would alter the material's electronic properties in such a way that its water-splitting performance would be improved. For example, according to their calculations, substituting cobalt for iron would reduce the energy of hydrogen adsorption on to the catalyst surface to the level of platinum at the optimal composition.



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Electrodes made from nanoporous iron–cobalt phosphide have the potential to split water for a fraction of the price of electrodes made from precious metals.

But although the calculations looked good, producing these alloys was a stumbling block. Traditional 'wet chemistry' methods of making alloys are unsuitable as they do not give the necessary control over the exact ratio of metals. Therefore, the researchers had to develop a novel two-step way of making them. Their process involves using an industrial technique called melt spinning to rapidly solidify the precursor alloys, controlling their composition, followed by electrochemical etching to dissolve metallic byproducts, leaving an iron–cobalt phosphide with nanoscale pores (see image) whose catalytic activity could be adjusted by fine-tuning the ratio of iron to cobalt.

The resulting electrocatalyst rivaled the performance of commercial water-splitting catalysts, but for a 20th of the price, according to Tan's estimate. The team is now investigating the possibility of using their new fabrication technique to make a whole range of nanoporous catalysts, which could be used for many energy- and environment-related applications.

1. Tan, Y., Wang, H., Liu, P., Shen, Y., Cheng, C., Hirata, A., Fujita, T., Tang, Z. & Chen, M. Versatile nanoporous bimetallic phosphides towards electrochemical water splitting. *Energy & Environmental Science* **9**, 2257–2261 (2016).

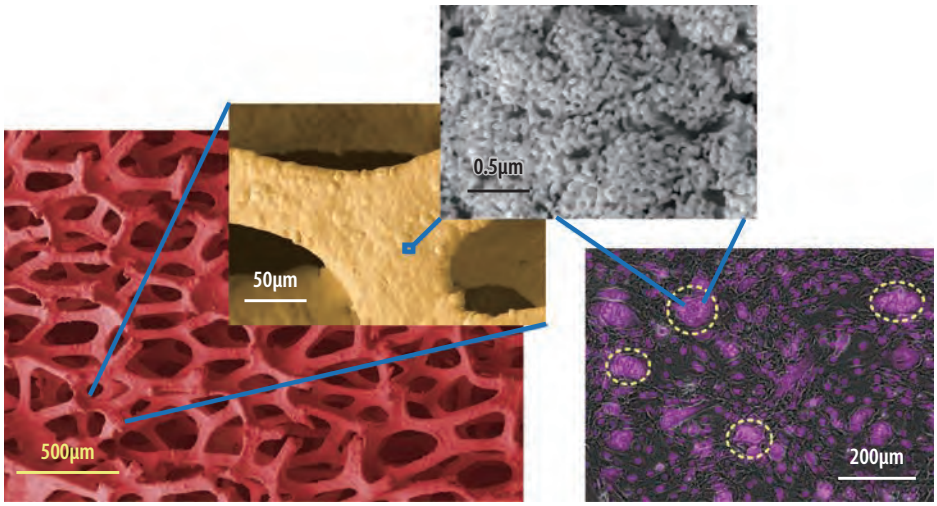
Nanoporous gold:

Sensitive biosensor for muscle chemicals

A gold film with both large and small holes can detect tiny amounts of chemicals released by muscle cells

By employing a gold film that contains multiple levels of pores, AIMR researchers have produced a sensitive detector capable of monitoring low levels of reactive chemicals that are released from muscles in the body. This detector is promising for advancing our understanding of the metabolism and functionality of skeletal muscle tissue.

Muscles attached to bones generate small amounts of reactive chemicals known as superoxide anions. Normal muscular activity generates low levels of superoxide anions, but high levels can be problematic since the species is quite toxic. "High levels of superoxide anions may trigger malfunctioning, aging and damage of muscle tissue," notes Ali Khademhosseini of the AIMR at Tohoku University.



A gold film that is porous on both a macroscale and a nanoscale has been used to realize a highly sensitive biosensor for detecting superoxide anions released by muscles. The pink regions in the fluorescence image on the far right indicate the nuclei of superoxide-releasing muscle cells.

Now, Khademhosseini and his coworkers have developed a highly sensitive detector that can detect very low levels of superoxide anions[1].

The genius of their detector lies in the fact that it uses a gold film that is porous on both macro- and nanoscales. Nanoporous gold is riddled with tiny pores and consequently has a high surface area. But, as Khademhosseini notes, "Although nanoporous gold has a large surface-to-volume ratio, only a small region of the film near the surface is exposed to the surrounding medium."

To overcome this problem, the researchers imparted the film with a high porosity on a macroscale by fabricating nanoporous gold films on templates of nickel foam, which contained macroscale pores (see image). This greatly increased the proportion of the film that is exposed to the medium. Since nickel is toxic to the body, the team chemically stripped the template away.

The scientists then demonstrated the effectiveness of the detector by coating it with an enzyme and then using it to measure the superoxide levels generated by muscle cells from mice. The biosensor realized a sensitivity that is two to three orders of magnitude higher than previous devices.

This high sensitivity makes the detector suitable for non-invasive measurements. "Since the physiological concentrations of superoxides are remarkably low, even sensitive electrochemical biosensors must be placed close to the region of interest, making them impractical for safe, *in vivo* operation," notes Khademhosseini. "Our sensor, on the other hand, can detect much lower levels of superoxides and thus can be placed farther from the site of injury."

The researchers intend to use their biosensor to investigate the rates at which superoxide anions are released when skeletal muscle tissue is subjected to electrical stimuli. They also anticipate that the multiple-porosity strategy used in the study will be applicable to a broad range of biosensing applications.

1. Sadeghian, R. B., Han, J., Ostrovidov, S., Salehi, S., Bahraminejad, B., Ahadian, S., Chen, M. & Khademhosseini, A. Macroporous mesh of nanoporous gold in electrochemical monitoring of superoxide release from skeletal muscle cells. *Biosensors and Bioelectronics* **88,** 41–47 (2017).

Single-cell analysis:

Double-barrelled probe for exploring single cells

A dual-action imaging and sampling technique promises rapid mapping of gene expression variation within single cells

A double-barrelled nanopipette is the secret behind a new technique for sampling messenger RNA (mRNA) at different locations within a cell. By filling the two barrels with different liquids, AIMR researchers used the same nanopipette as a microscope tip for imaging a sample of cells and then as a sample-collection tip for extracting mRNA from sites of interest identified during imaging[1].

After imaging the target cell, the team used the resulting map to take one messenger RNA sample from near the nucleus (left) and one from the cell's periphery (right; expanded image of the red box in the left image). The red crosses indicate the sampling points.

The device has the potential to become a high-throughput way to measure how gene expression varies within single cells. This information will give scientists a better understanding of how cells function in different tissues.

The double-barrelled approach, developed by Tomokazu Matsue, Hitoshi Shiku and their colleagues of the AIMR at Tohoku University, combines a pair of techniques for imaging and collecting samples from single cells.

The first step is an electrochemical imaging technique that involves sweeping a nanopipette filled with an aqueous solution across a sample. Applying a voltage to the tip causes ions to flow from the nanopipette tip, but ion flow decreases as the tip approaches and passes over a cell. Thus, by detecting the ion flow, it is possible to construct a topographical map of the sample.

"The microscopy imaging technique is non-invasive, so we can take images without any stress to living cells," says Shiku, leader of the project in Matsue's group. "We can scan the cell surface at low magnification and then zoom in to obtain higher-resolution images to find a location where we want to collect cytoplasm."

The team's advance was to then collect the cell's cytoplasm using the same electrochemical instrument. By using a double-barrelled pipette, the researchers could fill the second barrel. After lowering the pipette until it punctured the cell at the site of interest, the team switched the applied voltage from positive to negative, which drew a minute volume of cytoplasm into the nanopipette for analysis.

Testing the technique on living mouse cells, the researchers were able to take mRNA samples at the periphery and near the nucleus of single cells, revealing differences in gene expression between these two locations. The scientists also succeeded in fully automating pipette movement for the sample-collection process.

So far, the team has detected only highly expressed genes using their two-step technique. "The next stage is to improve the technique's sensitivity and increase the types and numbers of mRNA molecules we can sample," Shiku says. The team also plans to adapt the technique to detect proteins and organelles within cells.

1. Nashimoto, Y., Takahashi, Y., Zhou, Y., Ito, H., Ida, H., Ino, K., Matsue, T. & Shiku, H. Evaluation of mRNA localization using double barrel scanning ion conductance microscopy. *ACS Nano* **10,** 6915–6922 (2016).

INTERNATIONAL SYMPOSIUM

Published online on 28 March 2016

Mathematics and materials in harmony

AMIS2016 showcased potential real-world applications of fusion research involving mathematics and materials science

Since being appointed director of the AIMR in 2012, Motoko Kotani has led the charge in promoting collaboration between mathematics and materials science. To keep abreast of the fields' newest crossbreeds, researchers from all over the world travel to Sendai every February for the AIMR International Symposium (AMIS). This year's theme was 'harmonious collaboration between mathematics and materials science'.

"When we started this initiative, the distance between mathematics and materials science was very wide," explained Kotani. "But now materials scientists have started putting more emphasis in the direction of using mathematical modeling, information technology and data-driven science. To achieve this, direct interaction between mathematicians and materials scientists — experimental researchers in particular — is important. We just started this process a bit earlier."

Speakers at the three-day event on 22–24 February presented research on everything from tiny molecular machines that could one day power factories invisible to the naked eye, self-cleaning and antibacterial materials for glazing surfaces at hospitals and sports stadiums, to a fast-track route to developing new structural materials that will reduce our dependence on rare metals and rare-earth elements.

Upholding the legacy

Tohoku University President Susumu Satomi welcomed participants to the opening ceremony. More than 230 researchers representing 14 countries attended the symposium, including 22 invited speakers and 104 poster presenters. Satomi thanked Director Kotani and the AIMR for upholding a legacy of pioneering materials science and establishing extensive international networks. "The AIMR is expected to play a very important role toward achieving the goals of Tohoku University," he said, referring

The AIMR International Symposium (AMIS) 2016 offered a glimpse of what a world equipped with materials inspired by harmonious collaborations between mathematics and materials science would look like.

Theoretician Alexander Mikhailov uses simple and efficient models to describe complex cellular phenomena.

to the adoption of system reforms and the promotion of the university in global forums.

The next speaker was Toshio Kuroki, program director of the World Premier International Research Center Initiative (WPI), who disclosed plans to continue the prestigious national project. In 2014, a WPI program committee assessed that the five inaugural WPI centers, including the AIMR, had achieved 'world premier status'. As a result of their success, the government is discussing plans to continue the WPI program. The WPI program will also establish a grants scheme to support system reforms and internationalization activities in centers that have completed their ten-year term. The highly cited science and interdisciplinary research that exemplify the WPI brand will be sustained by the WPI centers and their host institutions — in the case of the AIMR, this will be through the newly established Organization for Advanced Studies.

AIMR Director Kotani promised to do her best "to keep the present activity of the AIMR as a world-leading hub of global brain circulation in materials science." In 2012, the AIMR initiated three target projects to strengthen ties between mathematics and materials science. In 2013, the AIMR introduced a fourth target project named Core Technology for Nano Energy Devices to translate the results of these harmonious collaborations into materials, devices and systems that will help solve global energy problems. AMIS2016 focused on this fourth target project and its practical applications, an area in which the AIMR has made significant progress through research into novel energy generation and storage materials, lithium-ion batteries, quantum-dot solar cells, thermoelectric conversion elements, nano-electronic switching devices and light-emitting diodes.

Chemist Akira Fujishima has discovered fascinating water-splitting and water-loving properties of titanium dioxide.

Simple science

A series of scientific presentations followed the opening remarks. Alexander Mikhailov, a theoretician at the Fritz Haber Institute of the Max Planck Society, presented his work on the use of mathematical models to explain, control and mimic complex phenomena such as those occurring in living cells. Packed inside the many cubic micrometers of a cell is a factory of nanoscale machines — motors, ion pumps and enzymes. These tiny biomolecules operate on millisecond timescales in extremely turbulent environments.

Teruo Kishi is director of a major government initiative to develop strong, lightweight and heat-resistant structural materials involving 27 industry partners, 35 universities and 130 scientists.

The chemical structure of these proteins is generally known, but their movement is harder to track. A popular but problematic technique involves running detailed molecular dynamics simulations of every atom in the protein. "Even using the best supercomputers, we can only follow the dynamics of a single protein for up to one microsecond, which is 10,000 times shorter than a single operation cycle," said Mikhailov. His group instead uses simple and efficient elastic network models that produce coarser representations of proteins as a series of amino acid 'beads' connected by elastic 'springs'. These models are so simple that they can run on a personal computer.

In 2010, Mikhailov's team used these models to identify how the hepatitis C virus helicase splits DNA — "the first structurally resolved simulation for a motor protein." More recently, the team has designed a molecular machine that swings forward using a ratchet mechanism similar to that used by actin and myosin filaments when a muscle contracts.

Presenting another material that mimics processes found in living organisms was renowned chemist and president of Tokyo University of Science, Akira Fujishima. He recounted his discovery in 1967 of titanium dioxide's ability to use light to split water like in photosynthetic plants; the results were published in *Nature* in 1972. Fujishima later found that titanium dioxide has a strong affinity for water and oils when irradiated by ultraviolet light. He has spent the last half century characterizing the photolytic, photocatalytic and superhydrophilic properties of this versatile material and developing affordable applications.

"Titanium dioxide is the best material — it's very cheap and safe and can be used to coat surfaces as a transparent film," he said. The material has been used to filter out the smell of cigarettes in bullet trains, maintain the stainless exteriors of train stations and football stadiums, prevent fogging of rear- and side-view mirrors, and kill bacteria and viruses that colonize hospital tiles. Fujishima is now trying to develop new applications for this material in water purification, solar light transmission and mosquito repellents. Meanwhile, scientific interest in titanium dioxide shows no sign of abating: close to 11,000 articles have cited Fujishima's original *Nature* paper according to the Web of Science and the number of publications on photocatalysis increases annually.

Next-generation materials

After a break, Teruo Kishi introduced several large-scale projects on structural materials funded by the Japan government to support the aviation, automobile and energy industries. Most recently, the Cabinet Office has set aside 3.5 billion yen to develop strong, lightweight and heat-resistant metals, alloys, ceramics, polymers and resins. These materials will reduce the energy and carbon footprint of air travel and power generation and make Japan less reliant on imports of rare-earth metals and other critical elements. As director of the Structural Materials for Innovation program, Kishi will manage a five-year collaboration between 27 industry partners, 35 universities and 130 scientists. He plans to integrate computer science and informatics with existing theoretical and experimental techniques in materials science to develop tools that can predict the performance of materials for rapid development and testing.

From big-picture science to a focus on synthesis, Kenichiro Itami, synthetic chemist and director of the WPI Institute of Transformative Bio-Molecules, presented his team's work on carbon-based nanomaterials. Nanocarbons have been a hot topic for fundamental research and applied science since the discovery of spherical fullerene in 1985, cylindrical carbon nanotubes in 1991 and graphene sheets in 2004, explained Itami. But these molecules are typically only available as mixtures of varying sizes, which means that their bulk properties represent an average of the individual molecules' properties.

Itami's group uses organic chemistry to create structurally uniform nanocarbons from flat or ring-shaped molecular templates, which could yield entirely new properties. "The beauty of science is purity," he said. Itami's team has since synthesized the shortest carbon nanotube with an armchair pattern, and accidentally synthesized a three-dimensional nanocarbon that has the negative curvature familiar to munchers of Pringles potato chips. The unique topology of the structure has even intrigued theoretical scientists. "Mathematicians are so excited about it," said Itami.

The opening session concluded with another chemist, AIMR principle investigator and president of the University of Science and Technology of China, Li-Jun Wan. His team focuses on the surface of materials, finding ways to assemble organic molecules in highly ordered patterns for potential application on functional devices, such as sensors. Specifically, Wan's group has laid out large sheets of graphene-like materials in which the individual molecules are connected via strong covalent bonds. "We really need mathematicians to join us to predict new structures and properties," said Wan. "I can find many collaborators at the AIMR to exchange ideas and results." ■

TOP-LEVEL INTERVIEW

Published online on 30 May 2016

A decade of remarkable achievement

This year, the AIMR marks ten years since its foundation. Former director Yoshinori Yamamoto and current director Motoko Kotani discuss AIMR's achievements over the past decade and its plans for the next stage of development.

Yamamoto: It's been ten years since the AIMR was established. It's a real milestone. It generally takes at least a decade to achieve something innovative.

Kotani: At the AIMR International Symposium 2016 in February, many participants told us that the AIMR has a sharp focus. We continually asked ourselves, "What is the AIMR's identity?" This helped define our focus. It seems that it takes at least ten years for something to take definite shape.

Former director of the AIMR, Professor Emeritus Yoshinori Yamamoto (left), and current director, Professor Motoko Kotani (right) discuss the AIMR's influence on the world of materials science and beyond.

Establishing AIMR's identity

Yamamoto: Initially, the AIMR's main focus was non-equilibrium materials, including metallic glasses — one of Tohoku University's strengths. Research was conducted by drawing on the expertise of physicists and chemists. However, we wanted to adopt a more innovative approach. We deliberated a lot about what we could do.

While staring at the crystal structures of some materials, I wondered whether there might be some connection with geometry. That was when I read your paper. I remember being surprised that a mathematician was discussing materials. I asked you to become director, but you were very hesitant initially.

Kotani: Yes, I hesitated at first. But after listening to the researchers and realizing that the director's role is to assist in defining the direction towards mobilizing research, I thought there might be something I could do here.

Yamamoto: I recall telling you that we want to apply mathematics to create a new kind of materials science. I managed to convince you of our vision, and you became director of the AIMR in 2012.

Kotani: I specialize in discrete geometric analysis, a branch of mathematics that analyzes how the discrete is linked to the continuous. The AIMR is investigating how discrete objects such as atoms and molecules control the continuous and large-scale phenomena of materials properties. It thus gave me a great sense of satisfaction to start working at the AIMR. The World Premier International Research Center Initiative (WPI Program) seeks to establish research institutions of excellence. We aimed to become a research center with exceptional originality, unparalleled in the world. Originality demands accepting the challenge of addressing something new.

You had set a very ambitious goal — to create a new kind of materials science. I imagine it was extremely difficult to define your concept clearly. It took five years to clarify the concept and another five years for it to take shape. The WPI Program gave us the opportunity to achieve this.

Yamamoto: You adopted three target projects. I believe these were crucial for coordinating and aligning materials science and mathematics.

Kotani: Yes. As you mentioned, Tohoku University is strong in non-equilibrium materials research. So I chose research into the use of mathematics to control non-equilibrium materials as target project 1. Since Tohoku University also excels in spin research, for target project 2, I selected research into topological materials (which is based on a branch of mathematics called topology) to investigate spin. Target project 3 was a project using my own specialist area, discrete geometric analysis, to understand hierarchical structures. These three projects drove the activities of the second five years.

Some researchers investigate the characteristics of a material out of interest in the material itself, whereas others search for a material that satisfies certain target functions. In mathematical terms, the first approach deals with a forward problem while the latter one deals with an inverse problem. The collaboration of materials science and mathematics at the AIMR means accelerating and streamlining the conversion of knowledge that has been accumulated as a forward problem into an inverse problem. This is the most critical reason why we need mathematics.

Providing pioneering researchers with an arena for success

Yamamoto: When MEXT announced the WPI Program ten years ago, I thought that it was wonderful. Japan suffers from its geographical position; our researchers have fewer opportunities for international exchange than their counterparts in Western countries. We applied for the WPI Program

because we wanted to become a research center with a highly visible global profile and achieve a global exchange of expertise, including researchers from Europe and America. Establishing the AIMR as a WPI center brought positive outcomes for Tohoku University and the wider world. Within Tohoku University, interaction increased rapidly beyond department and institution boundaries. In particular, young researchers now hold discussions that transcend disciplinary barriers. Beyond the university, the concept of materials science founded on mathematics is gradually propagating. Even MEXT is broadcasting it.

AIMR Director Motoko Kotani sees mathematics as a vital key for unlocking the mysteries of materials science.

Kotani: A huge achievement of the AIMR has been establishing a culture in which young researchers step out of their own laboratories and engage in lively discussions with researchers in other fields. And they see that this benefits their own research. When researchers from around the world visit the AIMR, they tell us that it differs totally from their image of a university. That means we have been motivating them to change their own research environment into something like what we have at the AIMR. We want to make it a spark that ignites a revolution of change in other universities. Leading on from the AIMR's experience, Tohoku University inaugurated the Organization for Advanced Studies last year.

Yamamoto: Interdisciplinary exchange has made great progress, but it's impossible to create a research center with a highly visible global profile overnight. After ten years, we have managed to make the AIMR highly visible.

Kotani: In the context of a research center with a highly visible global profile, it was you who gave me the idea of forming joint laboratories. You laid the groundwork for setting up joint labs with the University of Cambridge, the University of California at Santa Barbara and the Institute of Chemistry, Chinese Academy of Sciences. These AIMR Joint Research Centers (AJC) have raised the AIMR's visibility internationally. How did you come up with the concept of joint labs?

Yamamoto: I wanted to create a network with the world. I decided to choose attractive research institutions. Since Tohoku University is a world leader in materials science, I thought that our core partners should be universities that are world-leading centers for materials science and that have a history of academic exchange with Tohoku University. These three AJCs have certainly increased the visibility of the AIMR.

Kotani: The excellent quality of research in Japan is acknowledged globally. We have original ideas. I believe the reason that these are not necessarily reflected in the number of citations and world university ranking is that a lot of collaboration is undertaken as joint research within Japan. Since there are many outstanding researchers in Japan, we can obtain good results just by conducting joint research within our own country. But to achieve further advances, we need to incorporate new perspectives. That's the purpose of international joint research. The bridge between Japan and overseas is where young researchers can play an important role. The AJCs enable us to employ young researchers through joint arrangements between the AIMR and overseas centers. For instance, young researchers belonging to the Cambridge AJC are jointly employed by the AIMR and the University of Cambridge. Because they belong to both institutions, they can come and go freely between Sendai and Cambridge and do their research. This joint employment, formed by breaking systemic barriers, originates from your joint lab concept. Professor Alan Lindsay Greer, head of the Cambridge AJC, recently said to us that the University of Cambridge would like to provide research funding so that we can expand the AJC research activities.

Former AIMR Director Yoshinori Yamamoto came up with the concept of AIMR Joint Research Centers.

Yamamoto: Attracted by our idea, the historic University of Cambridge is thinking of extending the joint research center on their own. That is groundbreaking. Since such wide-ranging outcomes are being generated, we should really continue using the research center style adopted by the AIMR. Because the WPI Program establishes research centers, it also has to maintain them.

Kotani: After the initial sprint of ten years, the AIMR will now enter a new phase in which we will disseminate the results we have achieved. I have great hopes that young researchers, who have talked to researchers in different fields and discovered the benefit of original perspectives, will leave the AIMR to work in the wider world, extending their activities to the global arena. Ten years from now, when it is their turn to lead the scientific world, I think research of a totally different dimension will emerge. To provide an arena for researchers who take up the challenge to pioneer into a new realm of science, I think is where the AIMR will continue to offer its greatest value. ■

INTERNATIONAL SYMPOSIUM

Published online on 25 July 2016

Raising awareness in Europe

The joint participation of four WPI research centers at the 2016 Spring Meeting of the European Materials Research Society proved to be a rewarding experience for all involved

On 2–6 May, researchers from the Advanced Institute for Materials Research (AIMR) shared their innovative contributions for a sustainable future at the European Materials Research Society's (E-MRS) 2016 Spring Meeting in Lille, France. Researchers described advances in efficient solar electricity generation, high-capacity hydrogen storage and closed-loop energy systems to an attentive audience of global leaders from industry, government and academia.

The AIMR attended the E-MRS Spring Meeting together with a team of 30 members representing the World Premier International Research Center Initiative (WPI) and four of its research centers — the AIMR, the International Center for Materials Nanoarchitectonics (MANA), the Institute for Integrated Cell-Material Sciences (iCeMS) and the International Institute for Carbon-Neutral Energy Research (I^{2}CNER) — including WPI Program Director Toshio Kuroki and AIMR Director Motoko Kotani. "In 2014, we found that joint participation in the E-MRS Spring Meeting was a very effective way to boost our presence, so we decided to attend it together again this year to get further exposure in Europe," said Kotani.

The WPI program was launched in 2007 to create globally visible research centers in Japan that act as hubs for global brain circulation. One of the most effective ways to enhance the international presence of both the WPI program and the individual WPI centers is for centers to jointly participate in international meetings. The E-MRS 2016 Spring Meeting was the second time the four centers have jointly participated at the event in Lille and the fourth time they have jointly participated in international meetings.

Researchers at the reception held at the WPI exhibition booth enjoyed chatting with WPI researchers over Japanese food and drinks.

WPI exhibition booth and symposium

The WPI team coordinated their attendance at the E-MRS 2016 Spring Meeting through three separate venues: an outreach activity in the exhibition hall; a one-day WPI symposium; and presentations by WPI researchers at other symposia.

The WPI exhibition booth was manned from 3 to 5 May. As in 2014, it contained furniture decorated with traditional Japanese designs to pique the interest of European researchers. Posters about the WPI program and the four centers were displayed on panels, and brochures were distributed to passers-by. The WPI outreach team was allotted a one-hour time slot to host an exhibitor workshop in the evening of 3 May, followed by a reception. Current president of the E-MRS, Luisa Torsi, vice presidents, Gilles Dennler and George Kiriakidis, and immediate past president, Thomas Lippert, attended the workshop. Many European researchers, including executive committee members of the E-MRS, joined the reception, and enjoyed chatting with members from the WPI centers over Japanese food and drinks. The informal gathering was a great opportunity to inform attendees about the WPI One-day Symposium to be held the next day, and it also served to increase the exposure of WPI in Europe.

On 4 May, Masaru Tsukada, administrative director of the AIMR, and Tomonobu Nakayama, administrative director of MANA, organized and chaired the WPI One-day Symposium, which explored the functional assembly of nanomaterials and their potential applications in electronics, energy and biology. The WPI Program and the individual WPI centers were first briefly introduced: Kuroki spoke about the objectives, achievements and future prospects of the WPI program and AIMR Director Kotani, iCeMS Director Susumu Kitagawa, I^{2}CNER Director Petros Sofronis and MANA's Nakayama introduced their respective centers.

New insights into hydrogen materials

The symposium proceeded with a scientific session of nine talks by WPI researchers and some invited and contributed talks by speakers from outside the WPI centers. In the morning session chaired by Tsukada, two AIMR principal investigators and two European professors invited by the AIMR presented their recent research on hydrogen materials and solar cells.

Andreas Züttel, a physical chemist at the Swiss Federal Institute of Technology in Lausanne (EPFL) and director of the Laboratory of Materials for Renewable Energy, described the key challenge for hydrogen technology today — the

synthesis of hydrocarbons such as octane using only atmospheric carbon dioxide and hydrogen produced from renewable electricity. Achieving this recycle process will help resolve both environmental and energy demands. "Many hurdles must be overcome, for example, realizing large-scale electrolyzers, hydrogen storage and carbon dioxide adsorption," said Züttel. "A well-controlled reaction between hydrogen and carbon dioxide that produces a specific product is needed. But if we can complete this process, we can realize a whole-energy conversion cycle that doesn't produce any environmentally damaging discharges."

Züttel is a long-time collaborator with AIMR Principal Investigator Shin-ichi Orimo, and the two are well known for their experimental demonstration of the highest-capacity hydrogen storage material. At the session, Orimo introduced recent studies into the synthesis of materials known as hydrides that offer a compact vessel for storing hydrogen. He described new high-density hydrides using a CrH_7 pentagonal-bipyramidal anion, superionic conduction in B_nH_n-type hydrides with large cage-like units, and new all-solid-state rechargeable batteries, including lithium–sulfur batteries that have complex hydride electrolytes.

Andreas Züttel from the Swiss Federal Institute of Technology in Lausanne (EPFL) fields a question about his plan to realize a whole-energy conversion cycle.

Toward high-efficiency solar cells

Next up was AIMR Principal Investigator Seiji Samukawa, who described a technique for fabricating solar cells containing silicon quantum nanodots to improve the sunlight-to-energy conversion efficiency of the cells. His team used a biotemplate as an etching mask and a low-energy neutral beam to realize quantum dots that are defect free and smaller than 10 nanometers. Samukawa found the meeting particularly valuable as he was able to chat with collaborator Alain Fave, a photovoltaics researcher at the Lyon Institute of Nanotechnology, National Institute of Applied Sciences in Lyon (INSA-Lyon), and exchange information on recent progress in silicon solar cell experiments. "Participation at the E-MRS meeting has been a good opportunity to meet friends in Europe and consider future collaborations," said Samukawa.

Alain Fave from the National Institute of Applied Sciences in Lyon (INSA-Lyon), giving a talk at the WPI One-day Symposium.

Fave gave a talk on the design, fabrication and characterization of ultrathin-film crystalline silicon solar cells that trap light efficiently. A major cost of silicon solar cell technology is the amount of silicon used per watt-peak. Reducing the thickness of the crystalline silicon layer, however, decreases the amount of light it can absorb. A critical area of research in the field is the development of technologies that can curb these optical losses. To achieve this, the Lyon Institute of Nanotechnology, within the framework of a European project led by the nanoelectronics research institute IMEC, recently fabricated photonic crystals and pyramidal nanostructures on the surface of the silicon layer by combining laser holographic lithography, reactive-ion etching, inductively coupled plasma etching and chemical etching. "These are the first steps toward developing a future generation of photonic-crystal-assisted solar cells," Fave said. "We hope it will lead to the realization of high-efficiency solar cells."

Presentations at other symposia

AIMR researchers also gave oral and poster presentations at other symposia organized at the E-MRS. Alexander Shluger, a professor at the Department of Physics and Astronomy and the London Centre for Nanotechnology, University College London, and a principal investigator at the AIMR, presented a theoretical study into the effect of excess electrons in oxides on the creation of Frenkel defects, in which an atom is displaced from its lattice position to an 'interstitial' site lying between lattice points. In particular, Shluger's calculations indicate that excess electrons injected from electrodes can be trapped in deep states in amorphous silicon dioxide and hafnium dioxide (HfO_2) and form quasiparticles known as polarons and bipolarons. The formation of bipolarons facilitates the formation of Frenkel defects in these materials. In a poster session, Moloud Kaviani, an AIMR research associate in Shluger's group, presented related theoretical research with respect to intrinsic electron trapping in amorphous HfO_2. These results are important for understanding dielectric breakdown mechanisms in electronic devices and conductive filament formation in resistive random-access memory cells employing silicon and hafnium dioxide.

Two research associates from the AIMR group led by Principal Investigator Ali Khademhosseini — Sahar Salehi and Majid Ebrahimi — shared their work on engineering muscle tissue in the biomaterials session. And Akio Higo, an assistant professor from Samukawa's group, presented research into the room-temperature operation of gallium arsenide quantum nanodisk light-emitting diodes fabricated using a technique called dry nanoscale etching and regrowth by metal organic vapor-phase epitaxy. "I really enjoyed this joint participation at the E-MRS meeting and had many valuable interactions, which I've not experienced at conventional conferences," said Higo. ■

INTERNATIONAL EXCHANGE

Published online on 28 November 2016

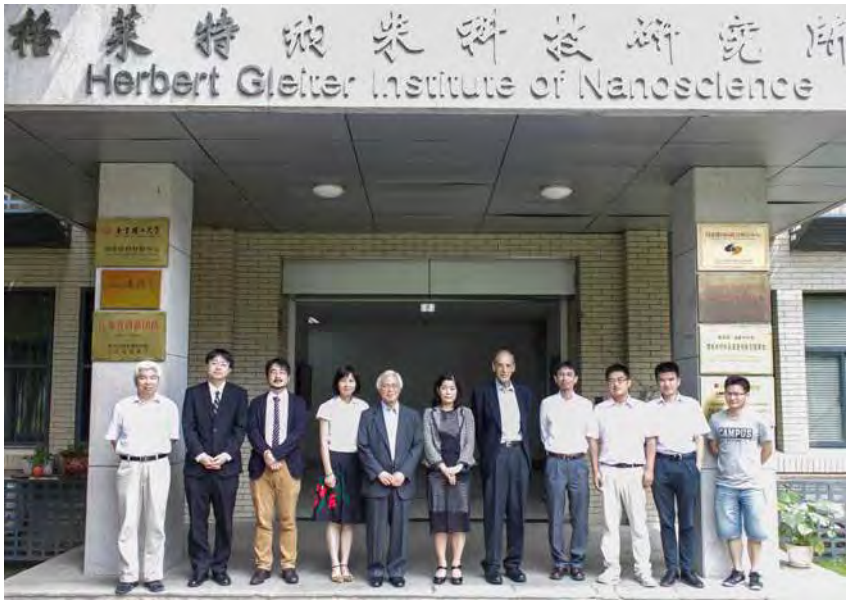
A new center of excellence in nanotechnology in China

AIMR researchers visited the Herbert Gleiter Institute of Nanoscience in China to exchange information and ideas

Herbert Gleiter was drawn to imperfections. At a time when most physicists were fixated on the perfectly ordered arrays of atoms in crystals, he got caught up in the defects, dislocations, grain boundaries and impurities. These deviations from a periodic arrangement of atoms, he noticed, gave materials interesting properties. By the 1980s, Gleiter had discovered a broad class of nanocrystalline — or nanostructured — materials, which contained a variety of irregular arrangements of atoms. This discovery laid the foundation for experimental and theoretical studies in an entirely new branch of nanotechnology.

In October 2012, Gleiter, who is on the international advisory board of the Advanced Institute for Materials Research (AIMR) in Japan, as well as a senior scientist and former founding director of the Institute of Nanotechnology at Karlsruhe Institute of Technology (KIT) in Germany, was invited to become the director of a new institute at Nanjing University of Science and Technology (NJUST). The Herbert Gleiter Institute of Nanoscience (HGI) focuses on research into nanostructured materials and devices, with a growing interest in an unusual type of glassy material known as nanoglass.

Mutual interests between the two institutes in China and Japan were the impetus for a visit by representatives of the AIMR in Sendai to HGI in Nanjing on 18 July 2016. The team included AIMR Director Motoko Kotani, Administrative Director Masaru Tsukada, Deputy Administrative Director Susumu Ikeda and several associate researchers.



A team of researchers from the Herbert Gleiter Institute of Nanoscience (HGI) and the Advanced Institute for Materials Research (AIMR) met in Nanjing to discuss mutual areas of interest.

Sendai to Nanjing

Gleiter kicked-off the exchange with an introductory presentation on the HGI. Five principal investigators lead three research themes at the institute: nanostructured crystalline and non-crystalline materials; chemical physics and functional nanobiosystems; and nanostructured metallic materials. HGI receives strong support from its host institution, NJUST, which is constructing a six-story building for the institute in Nanjing, a metropolis along the Yangtze River in eastern China. HGI is also expanding cooperation with NJUST, KIT, University of Münster, Shenyang National Laboratory for Materials Science and City University of Hong Kong.

Vice director of HGI, Jing Tao Wang, offered further details on the state-of-the-art facilities at HGI, which include a high-resolution scanning and transmission electron microscope, a scanning tunneling microscope, a helium-ion microscope and an X-ray computed tomography system with a spatial resolution of 50 nanometers.

Reciprocating these introductions, Kotani outlined the research activities at the AIMR, developments at the host institution, Tohoku University, and objectives of the World Premier International Research Center Initiative (WPI) program in Japan. She emphasized the collaboration between mathematicians and materials scientists at the AIMR and described current trends in data-driven materials science in the country, with a particular focus on the AIMR's role in these efforts, for example, through the Japanese government's Cross-ministerial Strategic Innovation Promotion Program (SIP).

Nanoglass and 3D graphene

The meeting in Nanjing offered researchers from both institutes a chance to share their latest scientific finds. Tao Feng, permanent scientist at the HGI, discussed a material first created by Gleiter and a team of researchers in Germany in 1989 — nanoglass.

Crystalline materials such as granite and quartz have been popular since the Neolithic age because of their predictability. Researchers can control their physical properties by tweaking their atomic structures. But materials with disordered atomic

structures, known as glasses, are much more difficult to manipulate. Nanoglass offers a way to control the chemical and physical structures of glasses due to its distinct nanostructures made of patches containing disordered clusters of atoms. Because the glassy regions do not quite match up where they meet, wide interfaces form between them, which influence the properties of the material. Feng described the techniques used to create these materials and some of their interesting thermal, magnetic and mechanical properties.

Glassy materials are also among the top areas of interest at the AIMR, and a strong source of collaboration between mathematicians and materials scientists. Recently, researchers have borrowed a mathematical concept known as topology to find hidden structures in the atomic arrangements of glasses.

Yoshikazu Ito, an associate professor at the AIMR, presented the result of three years of research into the development of another material with surprising abilities — highly crystalline, three-dimensional (3D) nanoporous graphene. The material behaves like two-dimensional, massless Dirac fermions, a characteristic previously not believed to be possible in 3D sheets of graphene. Ito is now trying to enhance the catalytic abilities of the 3D nanoporous graphene to facilitate the hydrogen evolution reaction in fuel cells. The material could be a promising alternative to noble metals such as platinum in realizing a hydrogen-fueled society.

Yoshikazu Ito, an associate professor at the AIMR, has created highly crystalline three-dimensional nanoporous graphene that could help to realize a hydrogen-fueled society.

Self-assembly

From novel materials to new ways of building them, permanent scientist at the HGI Qingmin Ji and associate professor at the AIMR Hiroshi Yabu shared their research into the spontaneous process by which structures form on the surface of materials, which gives them impressive abilities.

Ji recently joined HGI after working for several years in Japan at the University of Tsukuba, the National Institute of Advanced Industrial Science and Technology, and the National Institute for Materials Science. Ji's research focuses on the self-assembly of organic molecules on metal surfaces — useful for designing molecular machines — as well as the automatic formation of capsules of mesoporous silica, which could be used to gradually deliver drugs to the body over time.

Hiroshi Yabu, an associate professor at the AIMR, has used the power of self-organization to fabricate polymer nanostructures.

Yabu has used the power of self-organization to fabricate polymer nanostructures, including those inspired by the natural world. His talk focused on diblock copolymers, which are made of a string of one type of monomer interacting with a string of another type of monomer. When the two units come together, attractive and repulsive forces interact to produce structures containing different states of matter. Collaborating with mathematicians at the AIMR, Yabu has recently discovered that mathematical formulas known as Cahn–Hilliard equations can be used to predict these structures.

Zesheng You, a permanent scientist at HGI, has taken a different journey into the nanoscale. He specializes in a mechanical property of nanostructured materials known as fracturing. The way a material fractures largely depends on its geometry and size. You is developing new methods for measuring these properties in nanomaterials, which has led to some intriguing observations. For example, the fracture properties of polycrystalline materials depend on the size of the individual crystallites.

The exchange meeting in Nanjing concluded with a consensus to collaborate in mutual areas of interest and a tour of the advanced laboratories and facilities. The AIMR and HGI hope to maintain a friendly relationship through cooperation and healthy rivalry. ■

AIM*Research*

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