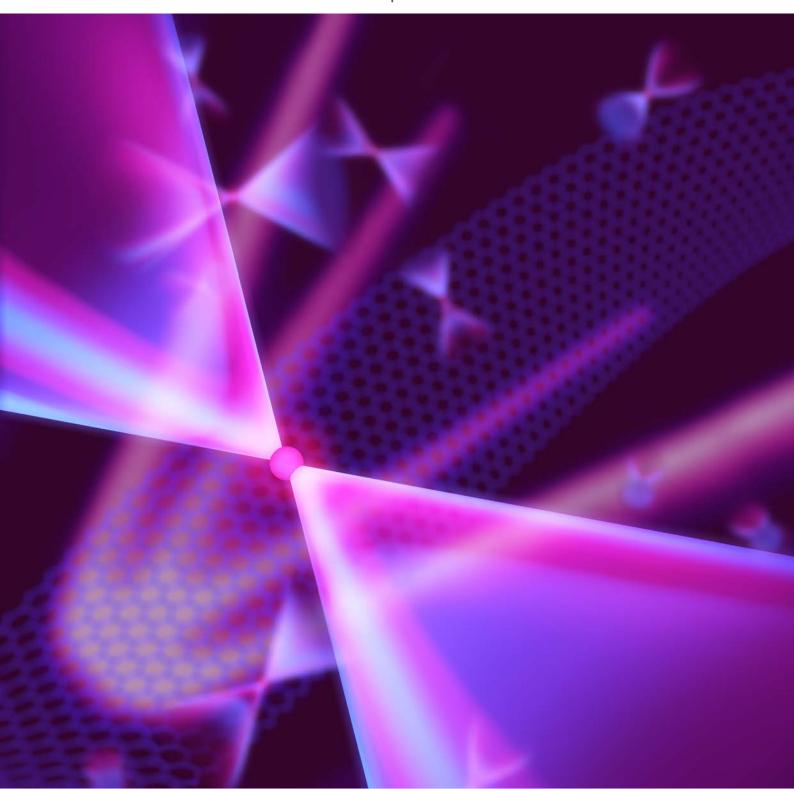
# AiN Research

### RESEARCH HIGHLIGHTS 2018 A publication of the WPI Advanced Institute for Materials Research









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#### WPI Advanced Institute for Materials Research

The Advanced Institute for Materials Research (AIMR) at Tohoku University in Sendai, Japan, was launched in 2007 as one of the centers established by the World Premier International Research Center Initiative (WPI) with the support of the Japanese Ministry of Education, Culture, Sports, Science and Technology (MEXT). Since then, the AIMR has been bringing together world-class researchers from Japan and abroad to carry out cuttingedge research in materials science through interdisciplinary collaboration among its four materials-related groups - Materials Physics, Non-equilibrium Materials, Soft Materials, Device/System - and the Mathematical Science Group.

In 2017, the AIMR became a member of the WPI Academy, which consists of WPI centers that have achieved worldpremier status. The institute will continue to maintain its world-class research environment and further promote global brain circulation.

Led by distinguished mathematician and director Motoko Kotani, the institute promotes interdisciplinary research across the different groups. It also fosters young researchers through the Global Intellectual Incubation and Integration Laboratory (GI<sup>3</sup> Lab). This unique program, which is currently supported by the WPI Academy, promotes international joint research conducted in close cooperation with high-profile researchers invited from countries around the world. The AIMR is host to about 100 leading researchers, around 40 percent of whom come from abroad, including 27 principal and junior principal investigators. In addition to the research hub at Tohoku University, the AIMR collaborates with research centers in China, Germany, Poland, the UK and the US. Close ties with other leading overseas institutes are maintained, going along with the efforts of foreign principal and junior principal investigators, as well as adjunct professors and associate professors.





## MESSAGE FROM THE DIRECTOR Establishing a truly global presence



The Advanced Institute for Materials Research (AIMR) was founded in 2007 with support from the World Premier International Research Center Initiative (WPI), a government program for creating world-class research centers in Japan. Since then, the AIMR has embraced the four WPI goals: advancing top-level research, establishing international research environments, reforming research organizations, and exploring new fields through interdisciplinary research. It has become a materials science center that attracts prominent researchers from around the world. From 2017, the AIMR has been promoting the global circulation of the world's best brains, while continuing to pursue world-class research as a member of the newly established WPI Academy.

An international hub for materials science, the AIMR promotes collaboration between mathematics and materials science. By using the universal language of mathematics to describe materials, which are extremely broad in scope, the institute is seeking to uncover commonalities between different materials and generate novel outcomes through new research themes. This initiative to get mathematicians and materials scientists collaborating on an institute level is rare and marks the AIMR as an advanced hub for materials science.

In June 2017, Tohoku University was selected as a Designated National University by the Japanese government, and it is expected to implement education and research activities of the highest levels in the world and contribute significantly to global development as a representative university of Japan. To enhance its research capabilities, the university is developing research centers in its four strongest fields: materials science, spintronics, next-generation medical care and disaster science. The AIMR is playing a central role in establishing the materials science center. In addition to launching five projects in the areas of energy materials, electronic materials, biomaterials, high-strength materials and structural control materials in collaboration with other departments, the AIMR is developing a system to promote fusion research among young researchers by overcoming boundaries between departments and between fields.

At the beginning of this year, more than 370 researchers from eight countries participated in the Kick-off Symposium for World-Leading Research Centers-Materials Science and Spintronics, which has jointly held with the new spintronics center in February 2018. The 25 distinguished invited speakers included Dan Shechtman, a chemist at the Israel Institute of Technology and Nobel laureate, David Awschalom, a physicist at the University of Chicago, and Alfio Quarteroni, a mathematician at the Polytechnic University of Milan and École Polytechnique Fédérale de Lausanne. To further accelerate the establishment of international networks based on the AIMR's pioneering research, the Tohoku-Purdue Workshop and the Tohoku-SG-Spin Workshop were held in conjunction with this symposium, followed by the 2018 AIMR Workshop. In addition, Tohoku-Tsinghua Joint Workshops were held in July 2018, and there were active discussions in the sessions on novel electronic materials and spintronics and on new structural and functional materials.

The AIMR is constantly engaged in exchanges with researchers and institutes outside of Japan. It participated in the European Materials Research Society held in France in June 2018 and ran a booth together with the other three materialsscience-based WPI centers. Many researchers visited the booth, which significantly promoted international exchange and international collaboration. The AIMR also organized a joint workshop with *Science and Technology of Advanced Materials*, an open-access materials science journal. Through such international events, the institute seeks to strengthen its global network and promote internationalization.

I would like to extend my sincere gratitude to everyone who has supported us. With the recognition of Tohoku University as a Designated National University, the AIMR aims to play a core role in developing its international research environment and to continue making advances in high-quality research. As a hub for the international circulation of the world's best brains, the AIMR aims to benefit society by advancing materials science.

Motoko Kotani, Director of AIMR

### **Graphene:**

# Opening up for the hydrogen economy

Observations of electron behavior when hydrogen atoms cram their way under graphene sheets could speed the development of fuel cells

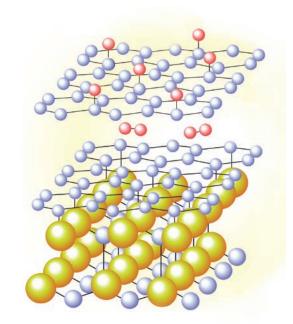
High-resolution spectroscopy by a team at the AIMR and Tohoku University has revealed how exposing graphene sheets layers of carbon just one atom thick — to hydrogen gas under controlled conditions can transform them into fuel-storage devices as well as produce magnetically active energy states<sup>1</sup>.

Chemists have long known that inserting atoms and ions into layered crystals, a process known as intercalation, can enhance ordinary materials. For example, many rechargeable batteries rely on intercalation of lithium within graphite to achieve stable power generation. Because the effects of introduced atoms are expected to be heightened for single-layer graphene, researchers are actively working to create devices based on intercalation.

A natural target for graphene intercalation is hydrogen. That is because theory predicts it can create band gaps in highconductivity graphene and produce the semiconductor-like properties needed for transistors and sensors. However, inserting lightweight hydrogen between carbon sheets requires careful adjustment, notes Katsuaki Sugawara from the AIMR.

"Because hydrogen's radius and bond lengths are so much smaller than those of graphene, it's hard to make it stay between the graphene layers," he says. "We worked to fix that by tuning the conditions of hydrogen exposure."

Sugawara and his team explored this problem using an analytical technique known as angle-resolved photoemission spectroscopy, which probes the electronic energy bands that hold solids together and shape their conductivity. By growing single graphene layers on silicon carbide wafers



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New electronic states that form when hydrogen atoms (red spheres) adsorb and squeeze underneath graphene layers (sheets of blue spheres) on a silicon carbide substrate (orange and blue spheres) could help develop band-gap-controlled high-speed transistors.

and pumping in hydrogen gas for specific times, they aimed to monitor changes to band gaps induced by the hydrogen atoms.

After optimizing temperatures for intercalation, the researchers observed that in pristine samples a new buffer layer of meshed carbon atoms appeared between the outer graphene sheet and the silicon carbide wafer. But longer exposures to hydrogen reduced the intensity of the buffer-layer energy bands and made bands associated with aromatic bonding in graphene more prominent — clear evidence that hydrogen atoms had entered between the layers and were disrupting existing chemical links (see image).

Further analysis of the band structure revealed that hydrogen exposure not only increased the available band gap for ballistic devices, but also created electronic states within the gap region. These states could tune the efficiency of ultrathin hydrogen fuel-storage devices or form a foundation for spintronic transistors, notes Sugawara.

"Theory predicts that the new gap states can introduce magnetic properties to hydrogen-adsorbed graphene," he states. "We want to elucidate which hydrogen additions are ferromagnetic and which lead to insulators."

Sugawara, K., Suzuki, K., Sato, M., Sato, T. & Takahashi, T. Enhancement of band gap and evolution of in-gap states in hydrogen-adsorbed monolayer graphene on SiC(0001). *Carbon* 124, 584–587 (2017).

## Metallic glasses: Non-uniformity uncovered

The source of the nanoscale non-uniformity in metallic glasses has been shown to be due to the existence of two distinct regions

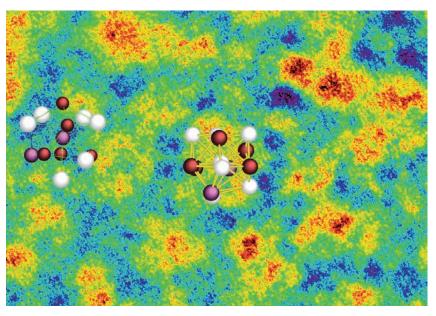
Using state-of-the-art analytical instruments, AIMR researchers have probed the nanoscale structure of a group of materials known as metallic glasses and discovered the origin of their nonuniformity on a nanometer scale for the first time<sup>1</sup>.

Metals generally have highly ordered crystalline structures. But under certain conditions, some form disordered, glass-like structures. Known as metallic glasses, these materials have intrigued materials scientists since they were first reported in 1960.

One aspect that has puzzled researchers is that, while metallic glasses have a random structure on a macroscale, nanoscale measurements have shown that their responses to stimuli vary at different sites on a sample. This indicates that metallic glasses are non-uniform on a nanoscale, but attempts to discover the reason for this non-uniformity had failed.

Now, by using scanning transmission electron microscopy and angstrom-beam electron diffraction, Akihiko Hirata of the AIMR at Tohoku University and his co-workers have found that metallic glass consists of two distinct regions on a nanoscale: dense regions, which have the order of a distorted 20-sided polygon (icosahedron), and less-dense regions, which are more disordered but still possess some crystal order (see image).

"It is extremely difficult to determine the structural differences between nanoscale regions using conventional X-ray, neutron or electron-scattering methods," says Hirata. "By utilizing the angstrom-beam electron diffraction developed by our group, we have been able to detect the local structure order of



This scanning transmission electron micrograph shows the two distinct regions in metallic glass: high-density regions (red areas) and low-density regions (blue areas). The crystal structures of the two regions have been superimposed.

spatial heterogeneity of metallic glass for the first time."

Discovering the nanostructure of metallic glasses is a key factor in determining their properties. "The grain size and dislocation density basically determine the strength and hardness of crystalline materials," says Hirata. "Metallic glasses, however, lack such key structural indicators due to their disordered amorphous structure. We believe that the spatial non-uniformity may play an important role in determining the mechanical and dynamic properties of metallic glasses."

The finding has significant implications for understanding metallic glasses. "Many intriguing phenomena of glassy materials stem from their complexity," says Hirata. "In a simplistic model, glassy materials are treated as being completely disordered. But our work has shown that at the nanoscale there are two distinct kinds of disorder in metallic glass. There must be an underlying mechanism for the formation of this disordered system."

In the future, the team intends to explore the effect of this non-uniformity on the mechanical properties of glass. They will also search to see whether the same non-uniformity exists in other metallic glasses.

Zhu, F., Hirata, A., Liu, P., Song, S., Tian, Y., Han, J., Fujita, T. & Chen, M. Correlation between local structure order and spatial heterogeneity in a metallic glass. *Physical Review Letters* **119**, 215501 (2017).

## Oxide materials: Fabricating 2D conductors

Understanding the electronic properties of a family of oxides could lead to the fabrication of two-dimensional conductors by sandwiching insulators between thin metal layers

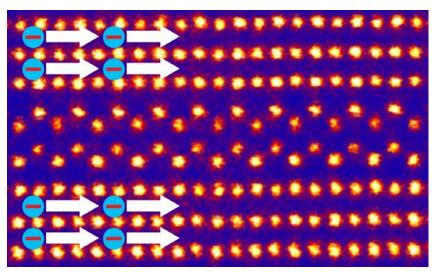
By using transmission electron microscopy and first-principles calculations, a team of AIMR researchers has elucidated the origin of electron transport in a class of crystals that could be engineered to realize materials that conduct electricity in just two dimensions<sup>1</sup>. Such twodimensional conductivity is promising for developing advanced electronic devices.

Solid oxides have been extensively studied by physicists and materials scientists alike because of the fascinating and useful properties that specific compounds can exhibit, including superconductivity, magnetism and ferroelectricity.

In particular, some oxide materials and structures exhibit electrical conductivity that is confined to two dimensions. One example is the family of compounds known as strontium niobates, which have the chemical formula  $Sr_nNb_nO_{3n+2}$ . Depending on the value of *n*, the members of this family can be conductors or insulators or exhibit quasi-one-dimensional conductivity (in other words, twodimensional conductivity that is nearly confined along a line).

"Materials with two-dimensional conductivity have potential applications for novel electronic devices, such as metal-oxide-semiconductor field-effect transistors and transistors with high electron mobilities," says Chunlin Chen, a researcher at the AIMR at Tohoku University.

To discover the cause of the unusual electrical behavior of  $Sr_nNb_nO_{3n+2}$ , a team led by Yuichi Ikuhara of the AIMR and Johannes Georg Bednorz of IBM Research – Zürich investigated the precise atomic and electronic configurations of various members of the family.



This scanning transmission electron micrograph shows zigzag-like slabs sandwiched between chain-like slabs where quasi-one dimensional conductivity can take place (indicated by the blue electrons and white arrows).

Scanning transmission electron microscopy revealed that each of these compounds consists of alternating stacks of zigzag-like and chain-like atomic slabs. The insulating or conductive behavior of the slabs depends on the valence of the niobium ions, which the team probed using a technique known as electron energy-loss spectroscopy. They discovered that zigzag-like slabs are insulating, whereas chain-like slabs are conducting.

Density functional theory calculations provided more insight into the origin of the insulating and conductive behaviors. Each slab has a backbone formed by NbO<sub>6</sub> octahedra. The electrons associated with the atoms in these octahedra can move along the crystals, thus contributing to the conductivity. However, the team found that the octahedra in zigzag slabs are severely distorted, inducing a localization of the associated electrons and hence insulating behavior.

Aside from providing fundamental insights into the electrical properties of these materials, the results show that two-dimensional conductivity can be obtained by inserting insulating layers inside conductors. The AIMR team will attempt this experimentally. "We will try to confirm the concept of segmenting a three-dimensional conductor into a stack of quasi-two-dimensional conducting thin layers by inserting insulating layers in other materials," says Chen.

Chen, C., Yin, D., Inoue, K., Lichtenberg, F., Ma, X., Ikuhara, Y. & Bednorz, J. G. Atomic-scale origin of the quasi-one-dimensional metallic conductivity in strontium niobates with perovskite-related layered structures. ACS Nano 11, 12519–12525 (2017).

## Nanoporous materials:

# A universal synthesis

A generic, green route offers an easy way to make an extensive range of useful holey materials with tunable pore sizes

The first universal route to materials containing extensive networks of tiny voids has been developed by AIMR researchers<sup>1</sup>. It is a highly controlled, environmentally friendly approach to make so-called nanoporous materials, which are finding a growing number of applications thanks to their lightness, high internal surface areas, high electrical and thermal conductivities, and fast mass transport.

"Nanoporous materials are being used as large-surface functional materials for applications such as supercapacitors, electrodes for lithium ion and lithiumair batteries, and plasmonic materials for molecular detection," explains Mingwei Chen, a lead researcher at the AIMR at Tohoku University and Johns Hopkins University, USA.

Typically, nanoporous materials are made using a process known as dealloying, which involves selectively removing one or more components from an alloy and leaving empty holes behind. But traditional electrochemical dealloying methods work on only a limited number of alloys and produce significant chemical waste.

In contrast, the novel vapor-phase dealloying approach developed by Chen's team can in principle be used to make nanoporous versions of all stable solid elements in the periodic table. Furthermore, it produces no chemical waste and even captures the components removed from the alloys. "These recovered materials are highly pure and can be reused to make alloys or surface coatings," says Chen.

His team built a bespoke dealloying system containing a high-temperature furnace, a vacuum system and a



Mingwei Chen and his team have developed a vapor-phase dealloying system that can be used to tune the size of the pores in a material.

condensation trap for capturing vaporized alloy components (see image). Using the cobalt–zinc alloy  $Co_5Zn_{21}$  as a model system, they explored the effects of varying the dealloying time, temperature and pressure on the size and location of the resulting pores. By tweaking these parameters, the researchers could tailor the size of cobalt's pores from tens of nanometers to micrometers. For example, lower pressures in conjunction with slightly lower temperatures resulted in an even network of copious, very small pores. The evaporated zinc was fully recovered from the trap.

Chen has demonstrated this technique on eight zinc-containing alloys. "These materials span from inorganic to metallic elements, lightweight to noble metals, low-melting-point elements to refractory metals," he says. The team is continuing to demonstrate the different nanoporous materials that can be made in this way.

"This is a scalable method for fabricating nanoporous materials," Chen adds. His team can currently make tens of centimeters of material at a time, but it should be possible to scale it up for industry applications. But Chen first wants to better understand the process. "We have started the basic research to understand the kinetics of nanopore formation and evolution during vaporphase dealloying."

Lu, Z., Li, C., Han, J., Zhang, F., Liu, P., Wang, H., Wang, Z., Cheng, C., Chen, L., Hirata, A. et al. Three-dimensional bicontinuous nanoporous materials by vapor phase dealloying. *Nature Communications* 9, 276 (2018).

## Lithium-ion batteries: Grinding out a better battery

By introducing atom deficiency, ball milling boosts the conductivity of a lithium borane material by 1,000 times, significantly enhancing its performance as a solid electrolyte

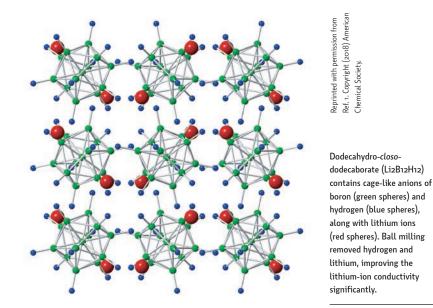
Simply grinding a lithium-based material can dramatically improve its conductivity, a study by AIMR and Tohoku University researchers has found<sup>1</sup>. This discovery could help to develop all-solidstate batteries that are safer and more efficient than conventional batteries.

Lithium-ion batteries are used to power everything from mobile devices to electric cars. Most commercial batteries use a liquid electrolyte to ferry charged lithium ions between the battery's electrodes during charging and discharging. But liquid electrolytes can leak and may be flammable, raising safety concerns.

Researchers are considering alternative solid electrolytes, including a family of materials known as *closo*-boranes. These materials have cage-like anions that contain boron, hydrogen and sometimes carbon. The spaces between these anions can act as conduction channels for lithium ions. But the anions also have strong bonds between boron and hydrogen atoms, making it difficult to modify the materials' structure to finetune their properties.

Sangryun Kim from the Institute of Material Research, Hiroyuki Oguchi from the AIMR at Tohoku University, and colleagues have now shown that introducing atom deficiency through ball milling — a method of mechanical grinding — can alter the structure of *closo*-boranes and enhance their conductivity.

They milled lithium dodecahydrocloso-dodecaborate  $(Li_2B_{12}H_{12})$  for 5 hours and then heated it to remove any trace of water. Analytical tests revealed that the material had lost lithium and hydrogen atoms and that some of



the remaining lithium ions had been rearranged in its crystal structure. Computer simulations of the material confirmed that relatively little energy was needed to free small amounts of lithium and hydrogen in this way.

These structural changes meant that the remaining lithium ions were better able to hop between vacant sites in the crystal structure, improving the lithium-ion conductivity. Indeed, further experiments showed that the ionic conductivity of the milled material was almost 1,000 times higher than that of unmilled material.

The researchers then used the milled material as an electrolyte in a battery, sandwiching it between a negative electrode made of lithium metal and a positive electrode made of titanium sulfide. The device maintained a good energy capacity over 20 charge–discharge cycles, whereas batteries that used unmilled material had a smaller energy capacity and a poorer capacity retention after cycling.

The researchers hope that milling could be used to tweak the composition of other materials based on cage-like anions. "We will investigate systematic routes to forming atom deficiencies as well as the precise relationship between atom deficiencies and lithium-ion conductivity," says Kim. "Based on these fundamental insights, we will try to develop high ion-conducting hydride materials."

Kim, S., Toyama, N., Oguchi, H., Sato, T., Takagi, S., Ikeshoji, T. & Orimo, S. Fast lithium-ion conduction in atom-deficient *closo*-type complex hydride solid electrolytes. *Chemistry of Materials* 30, 386-391 (2018).

# Encapsulation: Wrapping up in a hurry

A drop of liquid can be rapidly encapsulated in a polymer by simply being dropped onto a flexible film floating on water

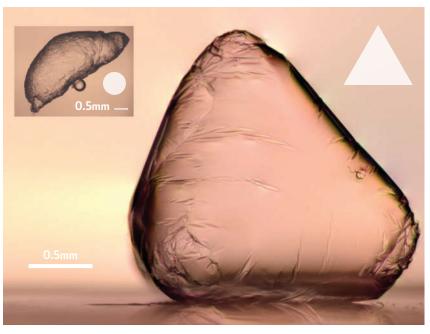
A fast, versatile and effective method to wrap liquids in thin polymer films, developed by an AIMR researcher and his collaborators, could be used to contain hazardous liquids and make containers for chemical reactants<sup>1</sup>.

Liquids are often encapsulated in other liquids; examples include emulsions used in the food industry and compounds for containing oil spills. But for some applications, a thin, solid wrapping would provide greater rigidity.

Now, Thomas Russell of the AIMR at Tohoku University, Narayanan Menon at the University of Massachusetts Amherst, along with two other collaborators in the USA, have devised a simple and elegant method that can encase liquid droplets in polymer films in a few tens of milliseconds.

Their straightforward technique involves simply releasing a drop of liquid from a specific height onto a small, thin polymer sheet floating on the surface of another liquid. As the drop sinks into the liquid, the polymer sheet wraps around it, encasing it completely. Surface tension ensures the seams that form in the polymer are nearly perfect with no gaps or overlaps.

Despite its simplicity, the method is highly versatile. Unlike conventional encapsulation strategies that generally produce only spherical droplets, the technique can produce capsules of different shapes by varying the shape of the polymer film (see image). Different combinations of liquids can be also used — in the study, the researchers performed wrapping by dropping both oil into water and water into oil. Russell notes that the approach could be



By using films of different shapes (triangle in the main image; circle in the inset), the encapsulation method can produce different shaped wrappings.

extended to other encapsulating materials: "In this study, we used a polymer to wrap liquids, but any thin sheet that is highly bendable, including thin metal sheets, for example, could be used."

The technique has many potential applications. "Since the sheets can be preconditioned or made from impermeable materials, they can easily be used to contain contaminants such as oil from a spill, toxic materials and highly reactive materials," says Russell. "Furthermore, multiple liquids that may react with each other can be wrapped separately, packed next to each other and stored. When it is time to use them, the wrappings can be broken and the contents allowed to react with each other." The team has plans to extend the study using more complex systems. "Since interfacial energy is driving the entire process, we are pursuing studies using bilayers where the interfacial interactions are different on the two sides of the composite sheet," says Russell. "We are also examining constructs where the bendability differs in different directions, for example in composites containing oriented rod-like fillers, like carbon nanotubes."

Kumar, D., Paulsen, J. D., Russell, T. P. & Menon, N. Wrapping with a splash: High-speed encapsulation with ultrathin sheets. *Science* 359, 775–778 (2018).

## Magnetic materials: Atoms near boundary determine magnetism

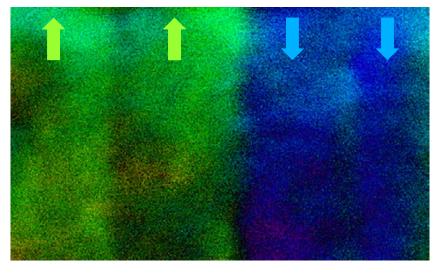
The relationship between magnetism and atomic structure at crystal boundaries in magnetite has been clarified for the first time

By employing the latest electron microscopy techniques and calculation methods, AIMR researchers have shed new light on magnetite, a magnetic material known since antiquity<sup>1</sup>. Specifically, they have shown that the magnetism at crystal boundaries in magnetite depends on the arrangement of atoms close to the boundary — an important finding that will inform the development of advanced magnetic devices.

Many magnetic materials are mosaics of small crystals whose magnetism points in different directions. A classic example is magnetite ( $Fe_3O_4$ ), the oldest known magnetic material. Material scientists have long wondered how the arrangement of atoms at the boundaries between these crystals relates to the crystals' magnetism, but it has been technically challenging to simultaneously and accurately determine both aspects.

Now, Chunlin Chen of the AIMR at Tohoku University and his co-workers have succeeded in doing this in magnetite by using state-of-the-art scanning transmission electron microscopy with differential phase contrast imaging to measure the electric and magnetic fields in the material. They also employed firstprinciples calculations.

The team, led by Yuichi Ikuhara, looked at a special kind of boundary between crystals in magnetite in which the atoms on one side of the boundary are a mirror image of those on the other side. They found that the magnetism in the crystals on either side of this 'twin boundary' can be either parallel (ferromagnetic) or antiparallel (antiferromagnetic; see image),



The magnetism in two adjacent crystals in magnetite as measured by scanning transmission electron microscopy. The magnetism is antiparallel in this case (as indicated by the green and blue arrows).

depending on the arrangement of atoms close to the boundary.

This was an unexpected discovery. "We were surprised to find that the magnetic coupling of twin boundaries depends only on the atomic core structures and resulting electronic structures within a few atomic layers of the boundary," says Chen. "We had previously thought that atoms far from the interface might also play an important role."

The finding is a significant one for the field. "Establishing the one-to-one correspondence between the atomic structure and magnetic coupling across individual boundaries has been long desired in the field of magnetism and magnetic materials," notes Chen.

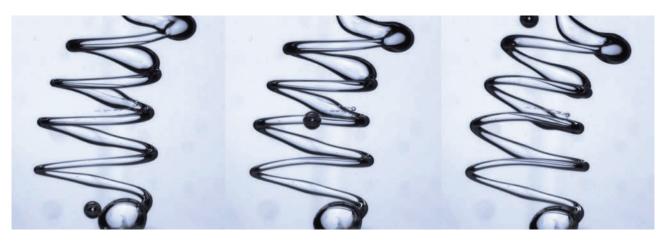
This insight will be valuable for practical applications, Chen says. "This tells us that we can tailor the magnetic properties of multilayer magnetic films by manipulating their interfacial microstructures, which will facilitate the development of high-performance devices."

The team now hopes to establish a general rule for the interaction between the atomic and electronic structures of magnetic materials and the magnetic properties of their grain boundaries by systematically investigating the magnetic couplings across other types of grain boundaries in magnetite.

Chen, C., Li, H., Seki, T., Yin, D., Sanchez-Santolino, G., Inoue, K., Shibata, N. & Ikuhara, Y. Direct determination of atomic structure and magnetic coupling of magnetite twin boundaries. ACS Nano 12, 2662–2668 (2018).

# Soft-matter physics: 3D printing a liquid into a liquid

A new three-dimensional printing technique allows stable water structures to be created within oil



A bubble rising through the center of a three-dimensionally printed spiral of water in oil.

In a study that broadens the potential of three-dimensional (3D) printing, scientists have modified a commercial 3D printer to print a liquid within another liquid for the first time<sup>1</sup>. This offers the opportunity to create new kinds of materials that could find a wide range of applications.

Until now, all printing has used either a solid or a liquid that solidifies on cooling. For example, printing a photo requires a solid paper-based substrate, while 3D printers often use liquid polymers that become solid on cooling.

Now, by three-dimensionally printing water within oil, a team led by Thomas Russell of the AIMR at Tohoku University has printed stable structures consisting of a liquid in another liquid. They added gold nanoparticles to the water and a surfactant to the oil. The nanoparticles and surfactant are attracted to each other, but, because of energy considerations, neither wants to leave the medium it is in. Consequently, they link up across the interface between the water and oil, forming a nanoparticle–surfactant layer that straddles this interface. Despite being only 20 nanometers thick, this layer is stable like a solid, but can readily deform.

"Conventional 3D printers produce solid materials like plastics, metals, hydrogels and even biological matter such as cells and organs," says first author Joe Forth at the Lawrence Berkeley National Laboratory, USA. "All these things are interesting and useful, but they're based on old paradigms. What's exciting about our technique is that it allows us to make a completely new type of material."

The researchers automated the process by modifying a commercial 3D printer. "We did everything on the cheap," recalls Forth. "We bought an entry-level 3D printer for printing plastics. We ripped out the printheads and replaced them with a syringe pump and some microfluidics tubing. If I could start over, I'd do it all differently, but what we did worked extremely well, given how little we knew about printing when we started." The new method opens a lot of possibilities. Since liquids can flow through these structures, they could be used in all-liquid microfluidic devices. Also, the printed aqueous shapes are promising as containers for living matter that can exchange chemicals across the oil-water interface.

"What's really interesting will be to see what the global scientific community can think of to do with a material like this, which combines soft-matter physics and nanotech to produce a material that's unlike anything else out there," says Forth.

The team is using their printed liquids to explore the mechanical properties of two-dimensional materials. They will also investigate how the materials behave when a magnetic field is applied to them.

Forth, J., Liu, X., Hasnain, J., Toor, A., Miszta, K., Shi, S., Geissler, P. L., Emrick, T., Helms, B. A. & Russell, T. P. Reconfigurable printed liquids. Advanced Materials **30**, 1707603 (2018).

## Charge density waves: Metal films mimic substrate's waves

The behavior of the electrons within an ultrathin metal film is affected by the electrons in the substrate it is on

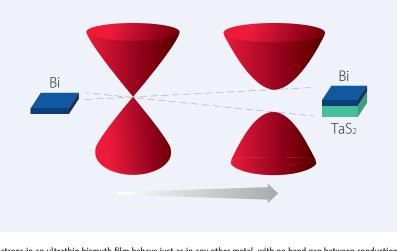
Electrons in an ultrathin metal layer sometimes adopt the same behavior as electrons in the underlying substrate, AIMR researchers have found. Specifically, electrons in a two-atomthick bismuth layer on tantalum sulfide (1*T*-TaS<sub>2</sub>) form a periodic formation known as charge density waves<sup>1</sup>. This finding offers a new way to control electrons in metal films and could have big implications for the application of topological materials to devices, such as field-effect transistors.

Interfaces between materials are of great interest to scientists because they often give rise to intriguing phenomena. In particular, a thin film on a substrate sometimes exhibits a property that the substrate possesses. For example, a metal film on a superconductor can become superconducting near the interface, and a nonmagnetic metal can become magnetic near its interface with a ferromagnetic material.

Now, Seigo Souma of the AIMR at Tohoku University and his co-workers have found that an analogous effect occurs for charge density waves — regular, wave-like arrangements of electrons that form in certain materials.

The researchers fabricated ultrathin films of bismuth on two substrates: silicon and 1T-TaS<sub>2</sub> (charge density waves form in 1T-TaS<sub>2</sub>, but not in silicon). They then examined the electronic states in the bismuth films using spectroscopy and calculations.

The team discovered that electrons in the bismuth layer on silicon showed no departure from normal behavior; in other words, the substrate did not affect



Electrons in an ultrathin bismuth film behave just as in any other metal, with no band gap between conduction and valence electrons (left). But electrons in a bismuth film on a 17-TaS2 substrate form charge density waves, which results in the formation of a band gap (right).

the bismuth. In contrast, they found that charge density waves formed in the bismuth layer on the 1T-TaS<sub>2</sub> substrate. Moreover, this resulted in the formation of a gap in the energy levels of conduction and bound electrons (see image) within the bismuth.

This effect may offer electrical engineers a new way to manipulate electrons in metals. "Our results demonstrate that this effect can be used to tune the electronic band structure in a bismuth film," explains Souma. "Since this effect opens up a relatively large energy gap, it will be useful for modifying the electronic states in films in contact with charge-densitywave materials. For example, this could be used to switch the energy gap in fieldeffect transistors."

The team now intends to grow more

complex compounds on 1*T*-TaS<sub>2</sub>. "We used bismuth in this study because it is a single element and relatively easy to grow," says Souma. "Next, we will grow films of topological insulators and semimetals and study the effect on them. If it turns out that charge density waves can be used to tune the band gap of a topological insulator or semimetal, it will be an important breakthrough for the application of topological materials to devices."

2018 Seigo Souma

Yamada, K., Souma, S., Yamauchi, K., Shimamura, N., Sugawara, K., Trang, C. X., Oguchi, T., Ueno, K., Takahashi, T. & Sato, T. Ultrathin bismuth film on 1T-TaS<sub>2</sub>: Structural transition and charge-density-wave proximity effect. *Nano Letters* 18, 3235–3240 (2018).

## **Block copolymers:**

# Mussels inspire magneto-optical film

By exploiting the multifunctional nature of a protein found in mussel feet, researchers have produced a hybrid film that exhibits useful magneto-optical properties

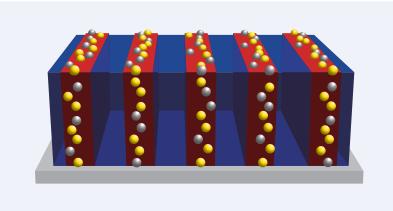
Inspired by a protein that helps mussels strongly cling to surfaces, AIMR researchers have devised a way to make a polymer film embedded with two kinds of nanoparticles: one plasmonic and the other magnetic<sup>1</sup>. This hybrid film is promising for imaging magnetic fields and for use in magneto-optical devices.

Mussels can adhere to a wide variety of materials due to the strong adhesion of mussel foot proteins. The main functional group of mussel foot proteins is catechol, which has strong adhesion and chemical reduction properties.

Now, Hiroshi Yabu of the AIMR at Tohoku University and colleagues have introduced this catechol group into a diblock polymer — a polymer made up of two alternating two building blocks (i.e., ABABAB..., where A and B are two chemical groups; for example, poly(vinyl catechol) and polystyrene in this study). "Only a few diblock copolymers containing the catechol group were reported prior to our study as catechol inhibits radical polymerization," notes Yabu.

The team next employed a two-step process that cleverly exploits the multifunctional properties of the catechol group to first add iron oxide nanoparticles and then silver nanoparticles to the diblock polymer (see image). The ability of catechol to include metal atoms in its structure enables it to incorporate the iron oxide nanoparticles, whereas catechol's reduction properties bring in the silver nanoparticles.

The combination of silver and iron oxide nanoparticles gives the hybrid polymer interesting properties. The iron oxide nanoparticles exhibit a phenomenon



A diblock polymer developed by Hiroshi Yabu's team at the AIMR consists of two building blocks poly(vinyl catechol) (red bands) and polystyrene (navy bands). Two types of nanoparticles — iron oxide nanoparticles (gold spheres) and silver (silver spheres) — incorporated in the poly(vinyl catechol) impart the film with special magneto-optical properties.

known as the magneto-optical Kerr effect (MOKE), while the silver nanoparticles enhance this effect by boosting the electromagnetic field in their vicinity. In the MOKE, the magnetic properties of a material alter the properties of light reflected from the material's surface, making it a powerful way to probe the local magnetization of materials.

"The MOKE is used in magnetic memory devices and future spintronics devices," says Yabu. "Our binary nanoparticle assembly enhanced MOKE signals by coassembly of plasmonic nanoparticles and magnetic nanoparticles, which opens the way to high density and highly sensitive magnetic devices."

The film could have much wider application by incorporating different pairs of nanoparticles. "This result indicates that our mussel-inspired diblock copolymer thin film is a promising platform for developing well-ordered hybrid thin films containing different nanoparticles," comments Yabu.

Yabu notes that the interdisciplinary environment at the AIMR was vital for developing the film. "This work is an example of the significant results from 'fusion research' between three laboratories at the AIMR working on polymer science, inorganic nanoparticles and spintronics," he says. Adapted with permission from Ref. 1. Copyright 2018 American Chemical Societ

Komiyama, H., Hojo, D., Suzuki, K. Z., Mizukami, S., Adschiri, T. & Yabu, H. Binary nanoparticles coassembly in bioinspired block copolymer films: A stepwise synthesis approach using multifunctional catechol groups and magnetooptical properties. ACS Applied Nano Materials 1, 1666–1674 (2018).

## Superconductors: Finding superconductivity in unexpected places

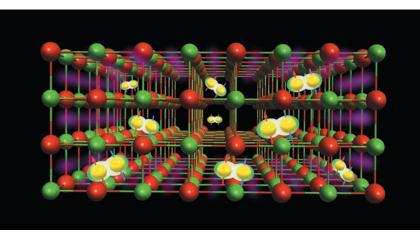
Thin films of a binary monoxide have been found to superconduct at a surprisingly high temperature

In an unexpected discovery, AIMR researchers have found that thin films of the compound lanthanum oxide (LaO) superconduct at temperatures below about 5 kelvin<sup>1</sup>. This opens up the possibility of using this oxide as a building block in novel superconductors made of superlattices — periodic structures consisting of layers of two or more materials.

Lanthanum oxide is not the most promising place to look for superconductivity. Samples made up of randomly orientated crystals were fabricated under high pressures in 1980 and found to conduct electricity like metals. The compound was largely forgotten about until high-temperature superconductivity was discovered in cuprate materials in the late 1980s. While one of these superconductors contained a molecular layer of lanthanum oxide, the layer itself was insulating.

Now, Tomoteru Fukumura of the AIMR at Tohoku University and his colleagues have made single-crystal thin films of rocksalt lanthanum oxide — so-called because it has the same crystal structure as sodium chloride, or common salt (see image) — and found that they superconduct.

"This discovery is both a surprise and a mystery," says Fukumura. "It is a surprise that such a simple binary monoxide is superconducting — so far, only two other binary monoxides have been found to be superconductors. And it is a mystery because only thin films with a single-crystalline structure show superconductivity; thin films made up of randomly orientated crystals don't exhibit



Thin films of rocksalt lanthanum oxide (lattice of red and green spheres) have been found to superconduct at temperatures below about 5 kelvin due to electrons forming Cooper pairs (yellow spheres).

superconductivity. We currently don't have a good answer for this difference."

The lanthanum oxide films superconduct at temperatures below about 5 kelvin (or -268 degrees Celsius). Although this does not sound very high, it is much higher than its cousins — other lanthanum monochalcogenides (that is, LaX, where X is sulfur, selenium or tellurium) all superconduct below 1.5 kelvin. It also bucks the trend established by these compounds: the temperature at which they start superconducting drops with decreasing mass, whereas lanthanum oxide, the lightest of them, has the highest superconducting transition temperature.

Fukumura's team also found that lanthanum oxide's transition temperature can be tuned by varying the strain in its crystal lattice.

The team is now trying to synthesize

other binary monoxides and their superlattices, since combining them with lanthanum oxide promises to open up exciting possibilities, Fukumura notes. "For example, europium oxide is a well-known ferromagnetic semiconductor. By combining lanthanum oxide and europium oxide, we should be able to make new ferromagnetic superconductors, which could be useful for superconducting spintronics." They have already succeeded in growing thin films of various rocksalt binary oxides, Fukumura adds. Such oxides could be used as building blocks for superlattices. D 2018 Kenichi Kaminaga

Kaminaga, K., Oka, D., Hasegawa, T. & Fukumura, T. Superconductivity of rock-salt structure LaO epitaxial thin film. *Journal of* the American Chemical Society 140, 6754–6757 (2018).

## Aromatic hydrocarbons: Polyacenes offer electronic surprises

Metal polyacene compounds have been surveyed for their magnetic and electrical properties, including superconductivity

After seven years of systematic study, AIMR researchers have found that a family of organic materials boasts some surprising electronic properties<sup>1</sup>. Their findings could have implications for research into high-temperature superconductors.

Carbon-based molecules are increasingly being used in electronic components such as transistors. These organic materials can be very sensitive to light, or electric and magnetic fields, and it is relatively easy to fine-tune their properties by chemically modifying them.

Some of these materials are based on hydrocarbons known as polyacenes. Their structures consist of benzene molecules joined in a linear chain. The simplest one, naphthalene, contains two benzene rings; adding more rings makes anthracene, tetracene and pentacene. Other hydrocarbons, such as picene and phenanthrene, contain similar chains in a zigzag pattern.

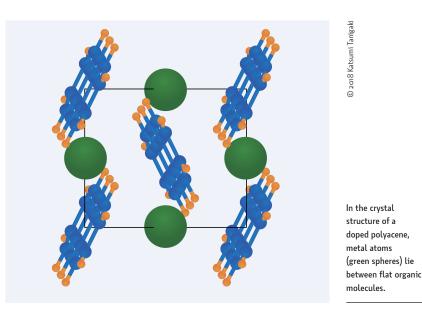
Researchers had previously reported that when metals are added to hydrocarbons like these — a process known as doping — the materials can carry an electrical current with no resistance, a property called superconductivity. However, there is considerable debate about this behavior.

Katsumi Tanigaki of the AIMR at Tohoku University and colleagues investigated the electronic properties of a range of these doped molecules. Yet multiple tests of potassium phenanthrene and potassium picene uncovered no superconductivity, contradicting earlier findings.

To further understand the behavior of these materials, the researchers developed a method for making doped polyacenes that produced higher quality crystals than had previously been available. X-ray diffraction measurements revealed that the potassium atoms in these compounds are trapped between flat planes of organic molecules (see image). This implies that the size of the metal atom will significantly affect the structure and properties of the crystal. Unlike potassium anthracene, for example, rubidium anthracene shows a form of magnetism, called paramagnetism, at room temperature.

Tanigaki's team also found that all of the doped polyacenes they studied are electrical insulators under normal conditions. However, while potassium tetracene and potassium pentacene are classical insulators, potassium anthracene and potassium naphthalene are Mott insulators, meaning that they can become conductors under certain circumstances. For example, the team found that the electrical resistance of potassium anthracene gradually declined as they ramped up the pressure. "We've succeeded in measuring intrinsic electrical transport systematically in doped polyacenes for the first time," notes Tanigaki.

The electrons in Mott insulators can interact in a similar way to how electrons behave in high-temperature superconductors, so these findings may offer valuable clues for further superconductivity studies. "Our studies of doped polyacenes from normal pressure to high pressure could provide important insights for future exploratory research of high-temperature superconductors," says Tanigaki.



Heguri, S. & Tanigaki, K. Carrier-doped aromatic hydrocarbons: a new platform in condensed matter chemistry and physics. *Dalton Transactions* 47, 2881–2895 (2018).

## Block copolymers: How to make virus-like nanoparticles

Nanoparticles that resemble viruses can be made by a facile technique

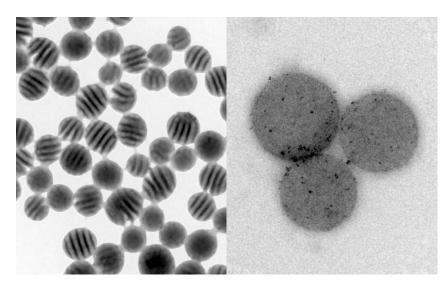
A simple but powerful technique for producing virus-like nanoparticles that have chemically 'patchy' surfaces has been developed by an AIMR researcher and collaborators<sup>1</sup>. Such nanoparticles promise to be useful for a wide range of applications, including cell delivery and photonic materials.

Viruses range in size from about 20 to 400 nanometers. Scientists have been able to create artificial nanoparticles in the same size range, but the surfaces of such nanoparticles are typically chemically uniform. In contrast, the surfaces of viruses are highly variable. Producing artificial nanoparticles that have chemically variable surfaces would greatly enhance their applicability in many areas.

"Chemically modified patchy nanoparticles are important not only for creating functional nanomaterials for efficient catalysts and biosensors, but also for enabling us to control the nanoscale features of synthetic polymer particles to be like a virus," says Hiroshi Yabu of the AIMR at Tohoku University.

Now, Yabu and colleagues have come up with a straightforward method for producing such chemically patchy nanoparticles. It involves dissolving molecules consisting of two different polymers, each with a functional chemical group attached, in an organic solvent. Since the polymers are hydrophobic, when water is added and the organic solvent is evaporated, the polymer molecules are forced together so that they form nanoparticles made up of the two polymers. They do this in such a way that molecules of the same polymer tend to clump together.

The distribution of the two polymers



Nanoparticles consisting of two polymers arranged in a stripy structure.

in the nanoparticles can be controlled by varying the preparation conditions. For example, stripy nanoparticles made up of alternating disks of polymers (see image), nanoparticles with circles on their surfaces, and nanoparticles with an onion-layer structure can be fabricated by varying the conditions, such as the polymer concentration.

By attaching a fluorescent dye to one of the polymers, the researchers were able to obtain images of the various nanoparticle structures.

"This method for producing functional nanostructured particles brings us one step closer to interfacial mimics of natural nanoparticles, and as such, may give access to interesting materials for fundamental biological studies or biotechnological uses," notes Yabu.

The functional chemical groups protrude from the surface of the

nanoparticles and can be easily modified through chemical reactions. This opens up a wide range of exciting possibilities. 2018 Hiroshi Yabu

The team plans to explore the potential of these nanoparticles. "We intend to chemically modify nanoparticles with enzymes and antibodies so that they can be used as biosensors for immunoassays and as intelligent drug carriers," says Yabu. "Furthermore, we hope to use them as templates for chemical catalysts that have arrays of different enzymes for realizing cascade reactions like those that occur in living bodies."

Varadharajan, D., Turgut, H., Lahann, J., Yabu,
H. & Delaittre, G. Surface-reactive patchy nanoparticles and nanodiscs prepared by tandem nanoprecipitation and internal phase separation. Advanced Functional Materials 28, 1800846 (2018).

## Colloidal nanocrystals: Mesostructured matter in a jam

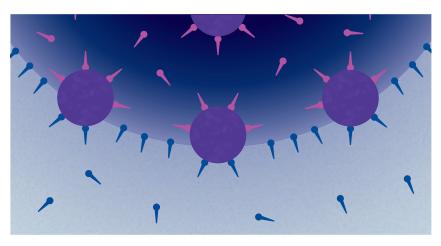
Soft magnetic actuators and all-liquid printed electronics are potential applications of nanocrystal assemblies that, when at an interface, can be switched between solid and liquid

A novel form of matter made from nanocrystals with tunable phase-changing properties at interfaces has been created by an AIMR researcher and his collaborators<sup>1</sup>. They used a tailored chemical additive to control the nanocrystal assembly's transition between the solid and liquid states. Applications for these dynamic materials range from catalysis and allliquid electronics to energy storage.

Although colloidal nanocrystals have been used to create many solid structures, nanocrystals that remain in a shape-shifting, liquid-like state have received much less attention, according to Thomas Russell, whose affiliations include the AIMR at Tohoku University, and Brett Helms from the Lawrence Berkeley National Laboratory, USA, who co-led the research.

"Our motivation was to devise a way by which two-dimensional assemblies of nanocrystals at interfaces can undergo solid-to-liquid phase transformations," Helms explains. When nanocrystal assemblies solidify they adopt a fixed shape, whereas nanocrystal liquids remain deformable with interesting dynamic properties. When these assemblies encapsulate liquids and retain their shape-shifting properties, a host of new applications become imaginable.

The researchers used positively charged iron oxide nanocrystals dispersed in a polar organic solvent and drawn into a syringe. They inserted the syringe tip into a second liquid consisting of amine-terminated poly(dimethylsiloxane) (PDMS-NH<sub>2</sub>) dissolved in poly(dimethylsiloxane) oil, and then extended a droplet of the nanocrystal dispersion from the syringe tip to create a well-defined interface between the two liquids.



© 2018 Thomas Russell

Small molecules (pink) surround the nanocrystals (purple), competing with amine-terminated poly(dimethylsiloxane) (blue) for binding to the nanocrystals.

The interesting chemistry happened at this interface, where the PDMS-NH<sub>2</sub> from one liquid would bind to the charged nanocrystals in the other to form a stable nanocrystal monolayer (see image) spanning the interface. When the monolayer was compressed by slightly retracting the droplet into the syringe, it 'jammed' into a solid state, creating a permanent wrinkled surface on the suspended droplet.

But the material's properties changed when the researchers added a charged small molecule to the polar organic phase, which could reversibly bind to the nanocrystals and compete with the binding of PDMS-NH<sub>2</sub> to the nanocrystals. When the droplet was retracted, the wrinkles appeared, but then disappeared, showing that the nanocrystal monolayer reconfigured back into its dynamic, liquid-like state. Thanks to the use of iron-based nanocrystals, the droplet also transiently deformed when an external magnetic field was applied. "In essence, we have created a soft magnetic actuator," Helms says. "In future schemes, the use of catalytically active nanocrystals would allow molecules encapsulated in the fluids to undergo chemical reactions." Such a system could function like a battery, allowing energy to be stored chemically and later released.

The team is continuing to explore the system's novel dynamic properties, Helms says. "Our next step is to translate the approach to three-dimensional printed objects from two immiscible fluids."

Zhang, Z., Jiang, Y., Huang, C., Chai, Y., Goldfine, E., Liu, F., Feng, W., Forth, J., Williams, T. E., Ashby, P. D., Russell, T. P. & Helms, B. A. Guiding kinetic trajectories between jammed and unjammed states in 2D colloidal nanocrystalpolymer assemblies with zwitterionic ligands. *Science Advances* 4, eaap8045 (2018).

## Metal oxide nanoparticles: Scrutinizing cerium oxide from all angles

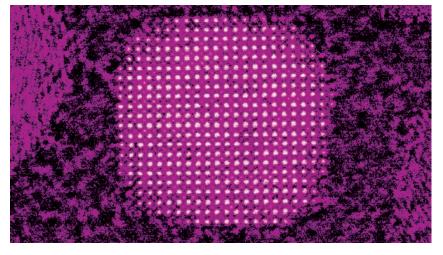
High-resolution analyses reveal the internal composition of cerium oxide nanoparticles and their interaction with individual surfactant molecules

By using state-of-the-art analysis techniques, AIMR researchers have mapped the distribution of valence states inside cerium oxide (CeO<sub>2</sub>) nanocubes<sup>1</sup> and imaged single surfactant molecules on the surfaces of cerium oxide nanocrystals<sup>2</sup>. These findings will help make moreefficient catalysts and pave the way to design new functional materials.

Cerium oxide is an extremely versatile ceramic, being used in applications as diverse as solid oxide fuel cells, catalytic antioxidants for treating oxidative stress-related diseases, and catalytic converters for cleaning vehicle exhaust gas. Most of its interesting properties, including its extraordinarily high capacity to store oxygen, stem from the fact that the cerium cation has two stable valence states,  $Ce^{4+}$  and  $Ce^{3+}$ , and can be repeatedly converted between them.

To gain insights into the mechanism behind the high oxygen storage capacity of cerium oxide nanocrystals, Yuichi Ikuhara and Tadafumi Adschiri of the AIMR at Tohoku University and colleagues used scanning transmission electron microscopy (STEM) and electron energy loss spectroscopy (EELS) to analyze the distribution of the two valence states within nanocubes of cerium oxide with sizes between about 5 and 12 nanometers. They discovered that, Ce3+ ions are concentrated near the surface of larger nanocubes but are almost absent in the center, where the Ce4+ valence state predominates. In contrast, nanocubes smaller than about 6 nanometers contain a significant amount of Ce<sup>3+</sup> ions at their centers.

These findings will inform both fundamental and applied studies. "Our



AIMR researchers have succeeded in imaging single surfactant molecules on the surfaces of metal oxide nanoparticles.

quantitative analysis of the valence state distribution, combined with local structural transformation, provides a basis for understanding the intrinsic features of cerium oxide nanocrystals," notes Adschiri. "It will also provide critical guidance for designing and fabricating novel oxygen-storage materials that can be used as catalysts and solid electrolytes."

In a related study, the researchers used STEM and EELS to examine how surfactants interact with cerium oxide nanoparticles. This is important since surfactants, which lower the nanocrystals' surface energy, are indispensable for synthesizing metal oxide nanoparticles with controllable sizes and desired morphologies and are thought to play a key role in applications. The team succeeded in imaging single surfactant molecules on the surfaces of metal oxide nanoparticles — the first time such a high resolution has been achieved. "We found direct evidence that surfactant coverage ensures the synthesis of well-dispersed ultrafine nanocrystals that do not clump together," comments Ikuhara. "The direct characterization of single surfactant molecules of an organic surfactant on the surfaces of metal oxide nanocrystals will advance our understanding of the surface chemistry of surfactant-modified nanocrystals."

The team will investigate the effect of adding dopants on the distribution of the valence state in ultrafine nanocrystals.

Hao, X., Yoko, A., Chen, C. *et al.* Atomic-scale valence state distribution inside ultrafine CeO2 nanocubes and its size dependence. *Small* 14, 1802915 (2018).

Hao, X., Chen, C., Saito, M. *et al.* Direct imaging for single molecular chain of surfactant on CeO2 nanocrystals. *Small* 14, 1801093 (2018).

## Superconductivity:

# A potential hide-out for Majorana fermions

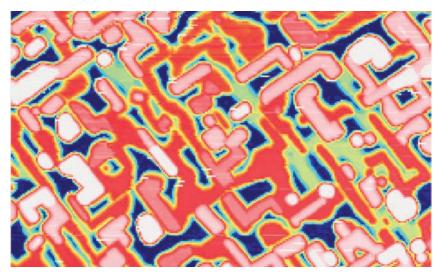
A hybrid material could be a good place to look for an elusive particle first predicted 80 years ago

A system created by AIMR researchers consisting of an ultrathin metal film on a high-temperature superconductor is a promising host for elusive particles known as Majorana fermions<sup>1</sup>. Such a platform could lead to new applications in spintronics and quantum computing.

Matter is made up of protons, neutrons and electrons, which are all examples of fermions — particles that have half-integer spins (for example, spins of 1/2 and 3/2). Every fermion has an antiparticle, which has the same mass as the particle but the opposite sign for one of its quantum properties (such as its charge). For instance, the antiparticle of the negatively charged electron is the positively charged positron.

Over eight decades ago, Italian theoretical physicist Ettore Majorana predicted the existence of a special fermion that is its own antiparticle, the so-called Majorana fermion. While Majorana fermions have yet to be observed as elementary particles, they could appear as quasiparticles — excitations in materials that behave as particles — in some special material systems.

So-called topological superconductors are particularly promising systems for supporting Majorana fermions. "The lowest energy state of topological superconductors has been theoretically predicted to form a superconducting gap in the electronic state of the bulk and gapless state at surfaces and edges, which should lead to the emergence of Majorana fermions," explains Katsuaki Sugawara of the AIMR at Tohoku University. "Consequently, many researchers are intensively studying topological superconductors with the goal of finding Majorana fermions."



A scanning tunneling micrograph of a candidate topological superconductor consisting of an ultrathin bismuth film on a high-temperature superconductor.

Now, Sugawara and colleagues have produced a hybrid material that they strongly suspect is a topological superconductor. They grew a six-atom-thick film of bismuth on top of a bismuth strontium calcium copper oxide superconductor and analyzed it using electron microscopy and spectroscopy techniques. Their analysis suggests that the hybrid material is a candidate topological superconductor. If it does turn out to be topological superconductor, there is a high chance it could be used to produce Majorana fermions.

Unlike other superconducting systems explored in previous studies, the one fabricated by Sugawara and his team superconducts at a high temperature and has a relatively large superconducting gap, both of which are advantageous for establishing it is a topological superconductor and for looking for Majorana fermions.

"We believe our new platform could harbor long-sought-after Majorana fermions that are stable at high temperatures," says Sugawara. "And it could help realize novel applications in spintronics and quantum computing."

The researchers are doing further experiments that will definitively show whether the system is a topological superconductor and can host Majorana fermions.

Shimamura, N., Sugawara, K., Sucharitakul, S., Souma, S., Iwaya, K., Nakayama, K., Trang, C. X., Yamauchi, K., Oguchi, T., Kudo, K. et al. Ultrathin bismuth film on high-temperature cuprate superconductor Bi<sub>2</sub>Sr<sub>2</sub>CaCu<sub>2</sub>O<sub>8+δ</sub> as a candidate of a topological superconductor. ACS Nano 12, 10977–10983 (2018).

# Deepening existing connections with Europe and Asia

The AIMR has been actively pursuing collaboration with researchers and institutions in both Europe and Asia

o enhance global awareness of the World Premier International Research Center Initiative (WPI) and four WPI materials-related centers, researchers from the Advanced Institute for Materials Research (AIMR) attended the 2018 European Materials Research Society (E-MRS) Spring Meeting in June, where they helped manage a booth and run a workshop. This was the third time that the four 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<sup>2</sup>CNER) — have jointly participated in the E-MRS Spring Meeting, which this year was held in Strasbourg, France.

The WPI exhibition booth provided an important platform to promote the activities of the WPI and the four centers to attendees of the 2018 E-MRS Spring Meeting. Over the three days that the booth was open, it attracted many European researchers, who browsed its posters and brochures while enjoying some traditional Japanese food and beverages. A wide range of researchers visited the booth - senior researchers who had stayed in Japan or had collaborated with Japanese researchers; young researchers interested in working at Japanese institutions; and participants from other booths who were curious about Japanese academic institutions. Outreach staff members from the four WPI centers managed the booth and were joined by WPI researchers between sessions. Such face-to-face dialog between WPI members and European researchers was very valuable for enhancing the profile of WPI and the four centers.



Top: Susumu Ikeda, director of the AIMR Research Support Division, introducing the workshop and the WPI at the STAM–WPI Joint Workshop. Bottom: The WPI exhibition booth at the 2018 E-MRS Spring Meeting in Strasbourg, France.

Also this year, the WPI centers held a joint workshop with the open-access materials science journal *Science and*  *Technology of Advanced Materials* (*STAM*) about future developments at the frontiers of materials science. This joint

workshop was born out of discussions held two years ago between members of WPI and STAM about the possibility of collaborating to highlight the activities of the entire material science community in Japan. At the beginning of the workshop, AIMR's Susumu Ikeda explained the purpose of the workshop and introduced the framework of the WPI. His talk was followed by an introduction to STAM by its editor-in-chief, Shu Yamaguchi of the University of Tokyo. This was followed by five presentations about how materials science can contribute to realizing a sustainable society by researchers from four WPI centers and Swiss Federal Laboratories for Materials Science and Technology (Empa).

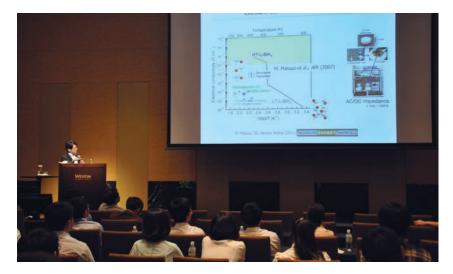
Hiroshi Yabu of AIMR talked about experimental and theoretical approaches for controlling the shapes of nanostructured particles made from polymers. His team has developed a simple method for fabricating block copolymer particles that have a variety of nanostructures by simple solvent evaporation from polymer solutions containing poor solvents. The unique phase-separated structures they obtained can be described by a mathematical model that was developed with the help of AIMR's mathematicians. This method can be used to create new nanostructured materials that will help address medical and environmental issues.

The four WPI centers have jointly participated in E-MRS Meetings every other year since 2014 as it is proving to be an effective way to promote international exchange and collaboration

#### Strengthening ties with Tsinghua University

Changing continents, the Tohoku– Tsinghua Joint Workshop on Materials and Spintronics Sciences is a good example of the effectiveness of promoting collaboration through long-standing efforts and mutual exchange with international partners.

The relationship between Tohoku University and Tsinghua University has been deepening over many years through active personnel exchanges — the two universities signed their first academic exchange agreement back in 1998. As part of Tohoku University, the AIMR has also cooperated with Tsinghua University. In



Shin-ichi Orimo, principal investigator at the AIMR, giving a keynote speech at the Tohoku-Tsinghua Joint Workshop on Materials and Spintronics Sciences in Sendai.

particular, Qikun Xue, vice-president and professor at the Department of Physics of Tsinghua University and principal investigator at the AIMR, has made a vital contribution by playing a leading role in the collaboration. He is also chair of the Tohoku University Alumni Association in China and has acted as a bridge between the universities as well as the AIMR.

An important way to strengthen collaboration is to establish common research themes with partners, which leads to two-way exchange of information and researchers. To build closer ties with partners in this way, the AIMR has established joint research centers at the University of Cambridge in the UK and the University of Chicago in the USA, and it is now in discussions with Tsinghua University to create another joint laboratory in Beijing, China.

In December 2017, the first joint workshop on materials and spintronics sciences was held at Tsinghua University as part of Tohoku University Day. Some AIMR researchers participated in the workshop and took the opportunity to discuss a plan to establish a new joint research center at Tsinghua University. This year, the AIMR organized the second inter-university event: The Tohoku-Tsinghua Joint Workshop on Materials and Spintronics Sciences. This was a key event in Tohoku University's new materials science research center, which is being established as part of the university's new status as a Designated National University.

On 26 July, after signing a memorandum of understanding, plenary lectures, and a tour of Takashi Takahashi's laboratory, the workshop was held at the Westin Hotel in Sendai. Both universities gave opening remarks, which were followed by two keynote speeches. Shin-ichi Orimo, of the AIMR and the Institute of Materials Research, Tohoku University, gave a talk on advanced hydride research for energy device applications, while Ke He of Tsinghua University described the search for intrinsic magnetic insulator materials.

Workshop participants then went to one of two parallel sessions: Novel Electronic Materials and Spintronics, and A New Stream of Structural and Functional Materials. Both sessions highlighted close interactions between the researchers at the two universities. Sometimes interactions went beyond research. For example, Jing-Feng Li of Tsinghua University obtained his PhD from Tohoku University in 1991 and worked at Tohoku University's School of Engineering until 2002. He has played a key role as a mediator in the exchange between researchers from the two universities. Several Tsinghua University researchers have also conducted research at Tohoku University.

Through these international events, AIMR is strengthening its global network and enhancing its internationalization, which is a key mission of the WPI centers. The AIMR is aiming for even greater heights, namely to become a dynamic hub for global brain circulation.



Hirano-Iwata in discussion with her laboratory staff. She finds the research environment at AIMR conducive to cooperative research.

#### FEATURED RESEARCHERS

Published online on 25 December 2018

# **Transcending research boundaries**

Drawing inspiration from Marie Curie and Japanese female scientists, AIMR principal investigator Ayumi Hirano-Iwata is exploring networks made from rat neurons as well as artificial cell membranes for detecting drug side effects

IMResearch talks to Ayumi Hirano-Iwata, a leading researcher at the Advanced Institute for Materials Research (AIMR) at Tohoku University. Her research straddles many fields, including bioelectronics and nanobiotechnology; she has also recently started collaborating with mathematicians. Hirano-Iwata joined Tohoku University in 2006, and in 2016 she became a principal investigator at the AIMR, which encourages researchers like her who want to overcome the boundaries

between research fields by adopting an interdisciplinary approach.

**AIMResearch:** It is not easy pursuing a career as female researcher in Japan. What led you to become a scientist?

**Hirano-lwata:** I remember being inspired after reading a book about Marie Curie when I was a middle school student. I struggled a bit when I started doing research as a university student as there were many things I didn't know. But after clearing that initial hurdle, I started to really enjoy generating my own conjectures — and the feeling of gratification when they turned out to be correct. It was hard to find research jobs after graduating. At first, I was just doing analytical chemistry and finding it a bit narrow and restrictive. I wanted to get into technologies that are more physics based. It was then that I joined Tohoku University, where I started doing research involving microfabrication and pharma-materials. And that research really took off.

## **AIMResearch:** What has been one of your career highlights?

**Hirano-lwata:** I've been working on developing artificial cell-membrane sensors that mimic actual heart cell membranes with a view to using them to detect potential side effects of drugs on the heart. Our artificial cell membranes were initially very fragile, making them almost impossible to use as sensors. So we tried stabilizing them using microfabrication techniques, and it worked very well. That was certainly one highlight.

We're continuing to work on them. Since drug side effects vary from person to person, we'd like to extend this approach for personalized medicine. If we can use microfabrication techniques to develop side-effect sensors tailored for individual patients, it will demonstrate the potential of using microfabrication for personalized medicine.

## **AIMResearch:** What other projects are you working on?

**Hirano-lwata:** I'm also leading a project in which we make circuits by taking neurons from rat brains and arranging them on small glass chips. These circuits are like miniature brains and they have functions that are beginning to resemble those of actual brains. In some cases, the circuits consist of just a few neurons, whereas in other cases we use about 100.

**AIMResearch:** Your research is interdisciplinary. What fields does it cover? **Hirano-lwata:** My research involves microfabrication, biomaterials, chemistry, electronic engineering, neuroscience and physiology. And I'm just starting a collaboration with mathematicians at the AIMR, including Hiroshi Suito, the leader of the Mathematical Science Group.

#### **AIMResearch:** Have you encountered any challenges in doing interdisciplinary research?

**Hirano-lwata:** Initially, it was difficult to communicate with each other. But sometimes even miscommunication can advance research. For example, when we were making the artificial cell membranes, the researchers responsible for fabricating microapertures didn't fully understand the biological aspects of the membranes. As a result, they made small tapered apertures. This 'mistake' turned out to be very



Ayumi Hirano-Iwata started her research life as an analytical chemist but is now doing research that straddles microfabrication, biomaterials, chemistry, electronic engineering, neuroscience and physiology.

effective in stabilizing the membranes. It was truly serendipitous.

## **AIMResearch:** How does the AIMR encourage interdisciplinary research?

**Hirano-lwata:** There are many research meetings that bring together scientists from different fields. For example, before joining the AIMR, I'd never been to a symposium by a mathematician. While working on fabricating artificial cell membranes at the AIMR, I was wrestling with how to figure out the best structure for our microfabricated chips to enhance the stability of the membranes, and I was beginning to despair that I'd ever be able to do it. But then I heard a presentation by a mathematician at an international symposium organized by the AIMR and I thought: "This person could solve the problem." So I spoke to him after the presentation, and he was very enthusiastic about collaborating with me. I've found that mathematicians at the AIMR are all eager to help, which is a real boon to researchers such as myself who are working on materials and devices. It really makes it easy to collaborate. Other AIMR researchers, such as junior principal investigator Hiroshi Yabu, are also working on the collaborative project to fuse biomaterials with mathematics.

**AIMResearch:** What kind of collaborations

do you have beyond Tohoku University? Hirano-lwata: I'm collaborating with a microfabrication scientist at Yamagata University and a protein researcher at Saitama University. A scientist at Toyohashi University of Technology is helping us characterize the artificial cell membranes. Overseas collaborations include one with Jordi Soriano at Barcelona University. He's an expert in the nervous system and is very good at analyzing the complex data generated by the neural circuits we make. Also, Tay Netoff of the University of Minnesota in the US is a specialist in small neural networks and we're working with him in constructing artificial networks of neurons.

# **AIMResearch:** As a female researcher, how do you find the research environment at the AIMR and Tohoku University?

**Hirano-lwata:** The situation has changed considerably since I was a student. I was lucky to become a PhD student as some professors wouldn't take women as PhD candidates. But the environment has changed to the point that sometimes being female can almost be advantageous. Tohoku University was the first university in Japan to admit female students, and it has developed a system for supporting female researchers and nurturing female leaders throughout the university.

## **AIMResearch:** Did you have any role models?

Hirano-lwata: Of course, Marie Curie was a big inspiration. In Japan, there was also Maki Kawai, who went to the same university as me. She has gone on to become a top researcher. She developed spatially selective single-molecule spectroscopy, and, in 2018, she became the first woman to become president of the Chemical Society of Japan. I aspire to be like her. Kaoru Tamada at Kyushu University who is a well-regarded professor was another good role model for me. Closer to home, there is Motoko Kotani, who leads the AIMR. It's a big encouragement having a female director at the institute who is also a top mathematician. She does a great job of leading the AIMR, while making efforts to create a research environment that is attractive for women, in keeping with Tohoku University's strong tradition of promoting female involvement in science.



**INTERNATIONAL SYMPOSIUM** 

Published online on 26 March 2018

# New beginnings in materials science and spintronics

A special symposium marked the commencement of an exciting new era in materials and spintronics research at Tohoku University

ollowing Tohoku University's selection by the Japanese government as a Designated National University in June 2017, plans are afoot to create world-leading research centers that will enhance the university's already formidable reputation in four vital areas: materials science, spintronics, next-generation medical care and disaster science. In collaboration with several other institutes and departments at the university, the Advanced Institute for

Materials Research (AIMR) will play a key role in developing the new materials science center.

To stimulate interdisciplinary dialogue and idea sharing, the Kick-off Symposium for World Leading Research Centers — the first event of its kind, being jointly organized by materials science and spintronics groups — was held in Sendai on 19–20 February 2018. It brought together top minds from Tohoku University and internationally, as well as industry partners. In his welcome address, Susumu Satomi, president of Tohoku University, spoke of the honor of being selected as a Designated National University alongside the University of Tokyo and Kyoto University. He highlighted the importance of strengthening research under this new framework and providing the best possible working conditions in the light of increasing global competition.

#### Engineering a social revolution

Representing Japan's Ministry of

Education, Culture, Sports, Science and Technology (MEXT), Masanori Shinano, deputy director-general of the Higher Education Bureau, conveyed his aspirations for "advancing research that will be a force for innovation and actualization of Society 5.0." Outlined in Japan's Fifth Science and Technology Basic Plan in 2016, Society 5.0 aims to transform society through the widespread adoption of artificial intelligence, big data, robotics and the Internet of Things (IoT).

Continuing on the theme of Society 5.0, Kazuo Kyuma, an executive member of Japan's Council for Science, Technology and Innovation, explained that "integrating cyberspace and physical space will be key to creating new values in industry and social systems" and novel materials will be indispensable to realizing this so-called Super Smart Society.

Kyuma expressed his confidence in the AIMR under the leadership of Director Motoko Kotani, highlighting its accomplishments in the areas of metallic glasses, porous materials and spintronics materials. He commended the impressive advances in spintronics by Hideo Ohno, director of the Research Institute of Electrical Communication (RIEC) as well as principal investigator at the AIMR, and Tetsuo Endoh, director of the Center for Innovative Integrated Electronic Systems (CIES).

#### Building on a proud legacy

In her opening remarks, Kotani referred to Tohoku University's more than century-long history of excellence in researching materials. It extends back to the founding of the Institute for Materials Research (IMR) in 1916 and the work of the institute's first director Kotaro Honda, who is renowned for his development of permanent magnet steels. It also includes the establishment of the Institute of Multidisciplinary Research for Advanced Materials (IMRAM) in 2001 and the AIMR in 2007.

Building on this rich history of research, the AIMR is exploring materials science by harnessing the power of mathematics, Kotani noted. She emphasized the importance of "forging strong international ties through a global alliance network, consolidating research capabilities at a university-wide level, focusing on research that addresses



Four plenary speakers at the symposium (clockwise from top left: David Awschalom, Alfio Quarteroni, Tetsuya Tsurumaru and Masato Sagawa).

the needs of society, and working toward the United Nations' Sustainable Development Goals."

Speaking in his capacity as RIEC director, Hideo Ohno, who will become the president of Tohoku University from April 2018, also reflected on the university's rich past. He drew attention to the work of Junichi Nishizawa, a pioneer in semiconductor research, and Shunichi Iwasaki, the inventor of perpendicular magnetic recording, a technology used globally in hard disks.

"Spintronics is a field that inherits and combines these early achievements," he said. Now spanning materials science, condensed-matter physics, device engineering and system applications, spintronics will be foundational for realizing Society 5.0, he added.

#### **Diverse technologies**

In a special message, Dan Shechtman, who was awarded the Nobel Prize in chemistry in 2011 for his work on quasicrystals, extended his congratulations to Tohoku University and expressed his hopes for young scientists to continue contributing to the university's outstanding achievements.

Presentations in six sessions began with plenary talks covering an array of new developments in spintronic technologies, mathematics, and computational and materials science.

David Awschalom of the University of Chicago explained that, in contrast to the conventional goal of removing defects from devices, his team is "putting defects back into quantum systems to explore new electronic and optical technologies." For example, embracing defects in silicon carbide to achieve a new level of control over spin dynamics could profoundly impact quantum information processing and medical imaging.

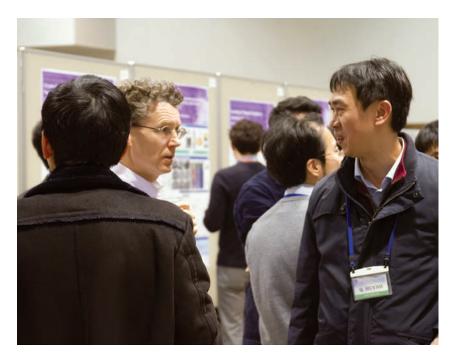
In his talk titled 'Taking Mathematics to Heart', Alfio Quarteroni of Politecnico di Milano, Italy, and the École Polytechnique Fédérale de Lausanne (EPFL), Switzerland, described how numerical simulations can be used to model systems even as complex as the human heart. Running simulations of healthy and unhealthy hearts, he said, could help doctors diagnose cardiovascular disease and determine better treatment plans. He added that mathematical models are providing insights into fields as diverse as seismology and sports science.

Representative director and chairman of Renesas Electronics Corporation, Tetsuya Tsurumaru, stated: "Spintronics has the highest possibility of providing solutions to emerging technological demands." Acknowledging the top-level spintronics research conducted at Tohoku University, he stressed the importance of strengthening mutual cooperation. "Semiconductors have the power to change the world," Tsurumaru said. The challenges ahead will be to "cultivate global human resources and encourage open innovation," he added.

Renowned inventor Masato Sagawa, now a consultant at Daido Steel Co, Ltd, presented his work on the development of neodymium-ironboron sintered magnets, for which he was awarded the Japan Prize in 2012. Referring to his studies at and later collaborations with Tohoku University, he noted that "the contribution of Tohoku University, especially that of the IMR, was overwhelmingly important in the evolution of the world's strongest permanent magnets." He indicated that the most promising applications for these magnets will be robots and electric vehicles, and concluded by proposing that the coming era of cleaner technologies based on light rare-earth elements such as neodymium be termed the Rare-Earth Iron Age.

#### **Projecting into the future**

In her presentation, after a brief introduction to the World Leading Research Center for Materials Science, Kotani gave an overview of the AIMR's activities so far and described her own expertise in geometrical analysis. She shared her vision for a collaborative way forward, which will be critical to achieving "new research objectives with increasing global relevance, including the



Researchers interacting at the symposium's poster session.

development of highly efficient energy conversion and storage systems based on functional materials, and reliable social infrastructure systems based on structural materials."

Kotani explained that the AIMR's three target projects have already proved fruitful, and said that mathematics as a common language is "helping to visualize, quantify and conceptualize data" to deepen our understanding of materials science.

On the university's new status, Kotani commented: "We are proud to be selected as a focus research center and more than happy to be a role model to transfer the know-how we have developed to achieve world premier status in the WPI program to other research centers." The AIMR, she adds, will aim to "maintain top-level research in its capacity as a member of the newly established WPI Academy and play a central role in Tohoku University's new materials science research center."

#### Unleashing the potential of spintronics

As the final plenary speaker, Ohno presented his work on nanospintronics

# "Semiconductors have the power to change the world."

devices for artificial intelligence and very large-scale integration. The ideal technology for working memory, he suggested, is a "non-volatile memory that is scalable and fast and has virtually infinite endurance." Spintronic memory devices, he averred, are the only ones known to be capable of achieving this ideal.

Ohno noted that scalability is one of the top priorities for industry to realize a wide variety of applications for artificial intelligence and that this aspect makes materials so crucial. The coming challenges, he said, will be to "deepen knowledge and transfer it to the real world and provide an R&D platform for cutting-edge technologies."

In total, 373 people took part in the two-day symposium, including 15 invited speakers, and 183 posters were displayed at Sendai International Center.

The symposium was followed by the AIMR Workshop 2018 on 21 February, which provided another opportunity for researchers at the AIMR, its joint research centers and overseas partner institutions to interact. Held annually since 2008, the workshop is a continuation of the AIMR International Symposium (AMIS), which aims to stimulate further research exchange and international networking at the AIMR through providing a forum for discussions from various angles.





#### AIMResearch

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

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