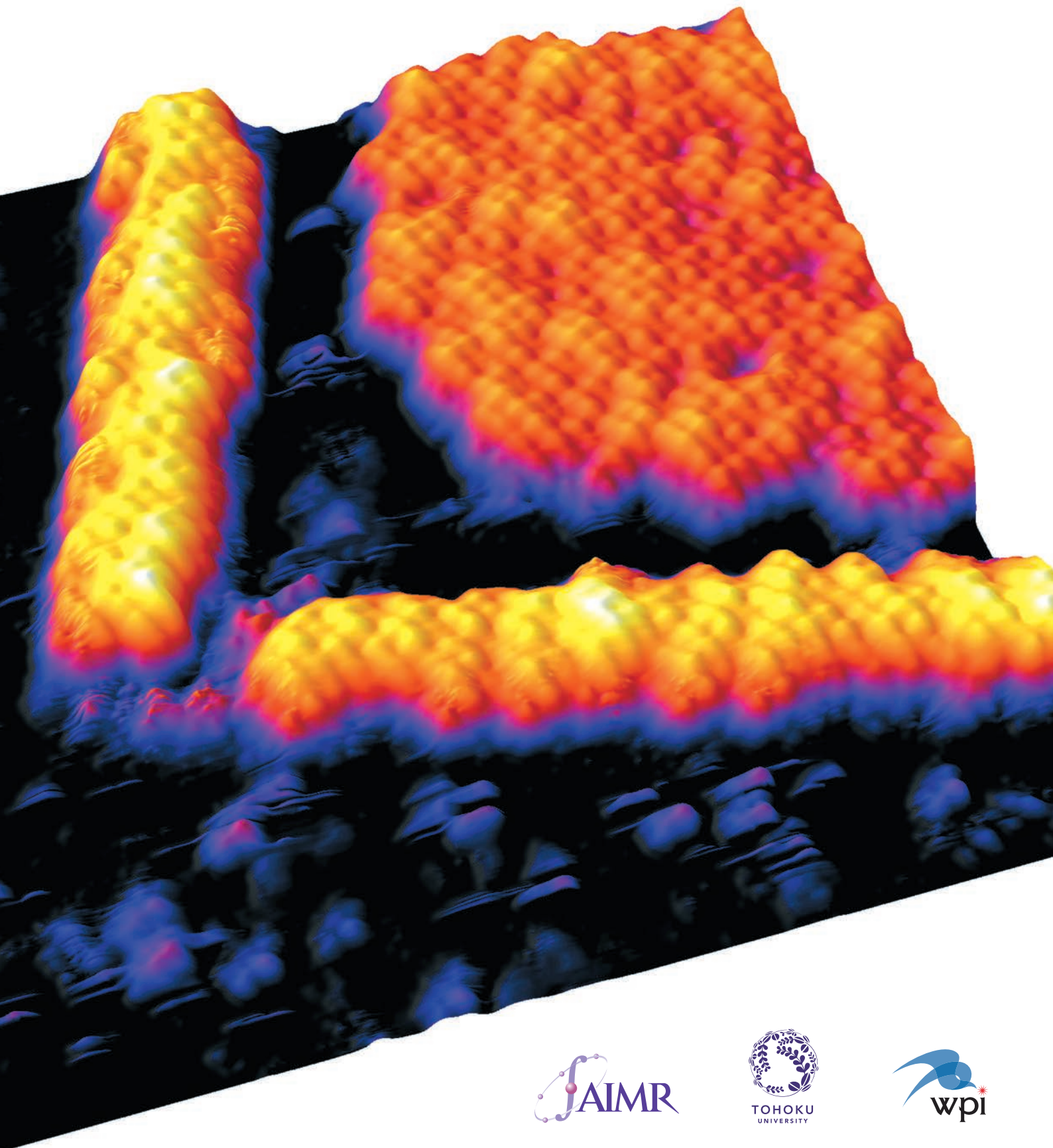


AiM Research

RESEARCH HIGHLIGHTS 2020

A publication of the WPI Advanced Institute for Materials Research

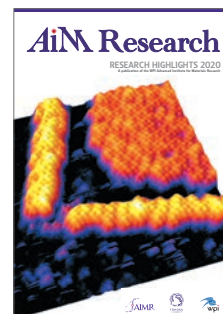


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COVER STORY

A three-dimensional image generated by topographic scanning tunneling microscopy of strontium vanadate nanowires formed on an ultrathin film of strontium vanadate (see page 13).

COVER IMAGE

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WPI Advanced Institute for Materials Research

Established in 2007 as part of the Japanese government's World Premier International Research Center Initiative (WPI), the Advanced Institute for Materials Research (AIMR) was tasked with pursuing world-class research and promoting global brain circulation. The AIMR has since been bringing together world-class researchers from Japan and abroad to carry out cutting-edge research in materials science through interdisciplinary collaboration among its four 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 world-premier status. The institute will continue to maintain its world-class research environment and further promote global brain circulation.

Led by distinguished material scientist and director Shin-ichi Orimo, the institute promotes interdisciplinary research across the different groups. It also fosters young researchers through the Global Intellectual Incubation and Integration Laboratory (GI³ 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 35 percent of whom come from abroad, including 26 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

An ambitious approach to materials science research



The Advanced Institute for Materials Research (AIMR) was founded in 2007 with support from the World Premier International Research Center Initiative (WPI), which was started by Japan's Ministry of Education, Culture, Sports, Science and Technology (MEXT) to set up world-class research centers in Japan. Since then, AIMR has advanced the WPI's four basic objectives: advancing top-level research, creating interdisciplinary domains, establishing international research environments, and reforming research organizations. As a result, it has established a research center for materials science that attracts outstanding researchers from all over the world. In 2017, AIMR became a member of the WPI Academy. It has upheld world-class research standards as it strives to accelerate and expand the global circulation of the world's best talent.

As an international center for materials science, AIMR has a key advantage in that it promotes collaboration between mathematics and materials science. By employing the universal language of mathematics to describe the extremely diverse field of materials science, we are endeavoring to identify the commonalities among a wide range of materials and to pursue new research fields with the goal of realizing novel outcomes. Even at the global level, initiatives such as this to foster collaboration among mathematicians and materials scientists throughout an entire research institute are rare; this undertaking is therefore illustrative of AIMR's status as a progressive center for materials science.

To further strengthen collaboration between mathematics and materials science, which lies at the core of AIMR's identity, we launched three new Advanced Target Projects in 2019, namely local structure control in topological functional materials; integrated control of bond variation and its time evolution; and improvement of self-organization technology and control of biological response. These ambitious projects seek to transform research into conventional static randomness into investigations of dynamic (or kinetic) randomness and to elucidate the responsiveness to external fields of hierarchical structures formed through self-ordering. AIMR researchers are also endeavoring to simultaneously study microscale perspectives (which are relevant to atomic and

molecular control technologies) and meso- and macro-scale perspectives (which are related to larger structures and performances), thereby accelerating material creation and the development of a diverse range of unprecedented physical properties and functionalities.

Furthermore, AIMR is promoting the use of the institute's angle-resolved photoemission spectrometer (which boasts the highest angular resolution in the world), scanning tunneling microscope, and the advanced measurement technologies available at the next-generation synchrotron facility, which is being built at the Tohoku University's Aobayama campus.

AIMR aims to adopt an approach that encompasses diverse advanced-material projects such as electronics, energy and biomedical technologies by leveraging advanced measurement technologies as well as collaboration between mathematics and materials science through the three Advanced Target Projects. Its scope will go beyond determining scientific principles, extending to the creation of materials that will benefit society. Strengthening collaborations with industry is thus one of the top priorities moving forward.

AIMR's approach of promoting collaboration between mathematics and materials science has attracted enormous interest from industry, particularly through programs such as Graduate-level Research in Industrial Projects for Students (g-RIPS). By promoting not just short-term results but also the creation of new materials through fundamental science, AIMR is committed to fulfilling its responsibility to be a research hub that benefits society through advanced materials science.

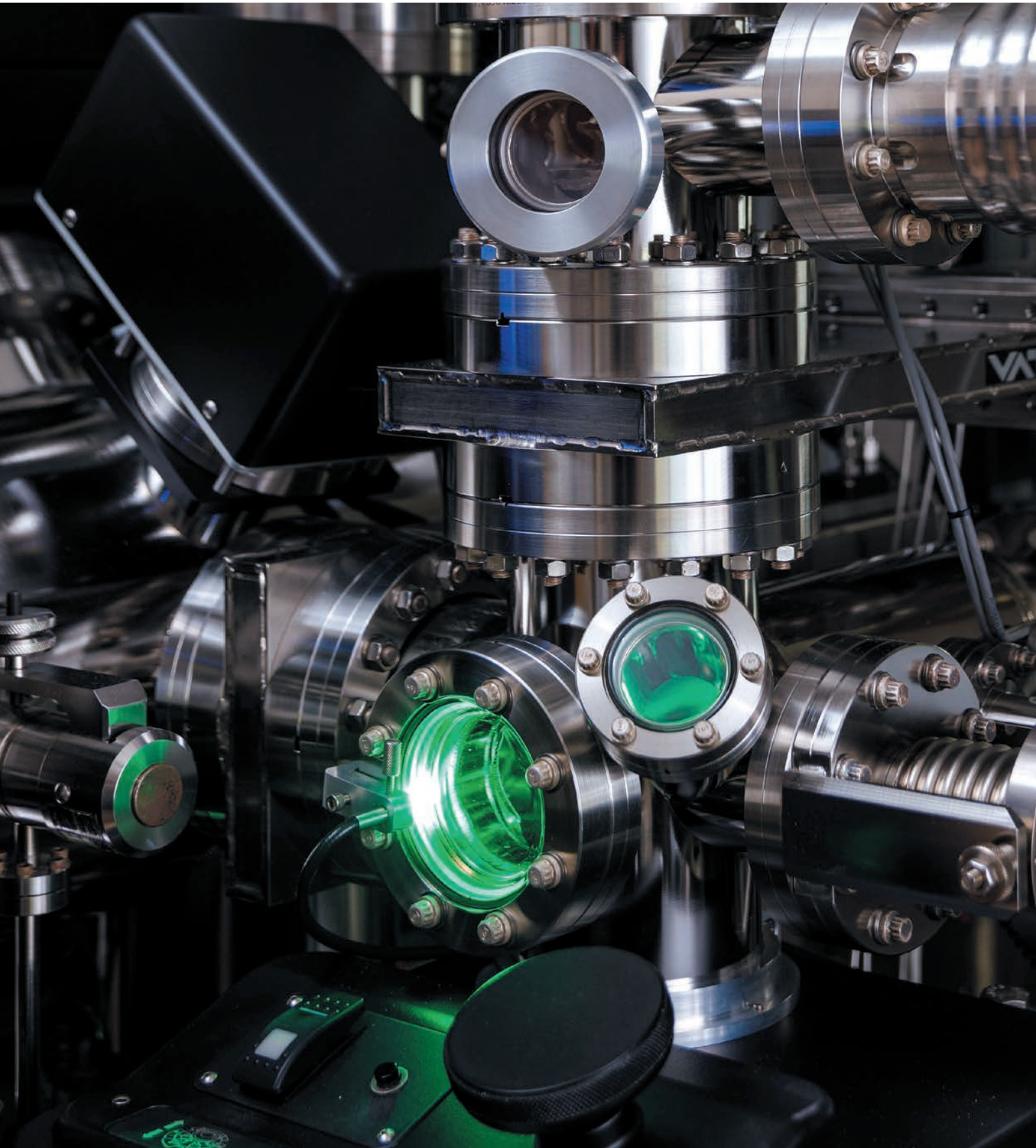
I would like to thank all those who have supported us. AIMR is playing a central role in Tohoku University's efforts to establish an international research environment as a Designated National University. At the same time, we intend to maintain our ongoing efforts to pursue high-quality research as a hub that facilitates the international circulation of the world's best minds and to contribute to cutting-edge materials science and global societal advancement.

Shin-ichi Orimo, Director

Advanced Institute for Materials Research, Tohoku University

RESEARCH HIGHLIGHTS

The AIMR advances research in materials physics, non-equilibrium materials, soft materials and devices/systems, and actively promotes collaboration among these divisions toward the development of ground-breaking technologies that cross the boundaries of conventional fields of study – bridging the disciplines of materials science, physics, chemistry and precision, mechanical, electronics and information engineering. The Mathematical Science Group further complements the AIMR's research activities.



LITHIUM-ION BATTERIES

Published online on 27 January 2020

Imaging a critical component of batteries

A powerful microscopy technique reveals new insights into the least understood part of lithium-ion batteries

Researchers at the AIMR have observed how an ultrathin layer on the negative electrode (anode) of lithium-ion batteries forms, grows and fails during battery operation¹. The important insights they have gleaned will be useful for developing better and safer lithium-ion batteries.

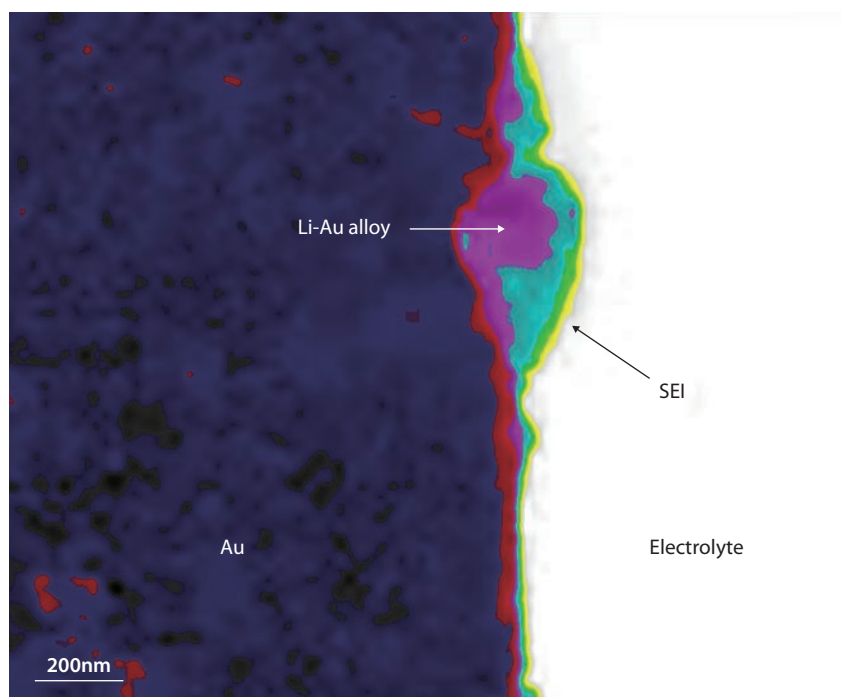
Lithium-ion batteries power everything from smart phones to electric vehicles. First commercialized about 30 years ago, they are a mature technology that has been intensively studied and developed. However, one of the most important but least understood aspects of lithium-ion batteries is an ultrathin layer — the solid electrolyte interphase (SEI) — that grows on the anode and protects it.

The SEI forms during the first few charge–discharge cycles and protects the anode from further decomposition. Although only a few tens of nanometers thick, the layer has a major effect on battery operation, notes Mingwei Chen at the AIMR of Tohoku University. “The SEI is one of the key factors that determine the safety, power capability and cycle life of lithium-ion batteries.”

One reason why the SEI is not well understood is because it is difficult to observe during battery operation.

Now, Chen and his group members have used a state-of-the-art scanning transmission electron microscope to observe how the SEI evolves during charging and discharging in a specially designed liquid cell that closely mimics the conditions inside a battery.

The researchers were able to image at a sub-nanometer resolution, which allowed them to see structures made up of inorganic and organic layers in the SEI (see image). “We were surprised that our scanning



An ABF-STEM image showing the formation of SEI films with a bilayer structure on the surface of an Au electrode undergoing Li-Au alloying reactions.

transmission electron microscope technique allowed us to clearly resolve the bilayer structures of the SEI,” explains Chen. These structures strongly suggest that the SEI grows through chemical reduction of the electrolyte at the boundary between the anode and the electrolyte. The team found that the growth of the SEI is also assisted by radical species that may form during the beginning stages of charging and discharging.

Chen and his co-workers also discovered that the SEI fails when it breaks and the inorganic layers come into contact with and rapidly dissolve in the electrolyte.

These findings will help researchers to

improve lithium-ion batteries. “The microscopic insights we have obtained have important implications for understanding the kinetics of the SEI and for developing high-performance anodes that are protected by robust SEI films,” says Chen.

In the future, Chen’s team intends to further investigate the effect of electrolyte additives on the formation of robust SEI films.

1. Hou, C., Han, J., Liu, P., Yang, C., Huang, G., Fujita, T., Hirata, A. & Chen, M. Operando observations of SEI film evolution by mass-sensitive scanning transmission electron microscopy. *Advanced Energy Materials* **9**, 1902675 (2019).

Nanoparticles with glass-like structure coalesce faster

Metallic glass nanoparticles merge with each other faster than crystalline nanoparticles

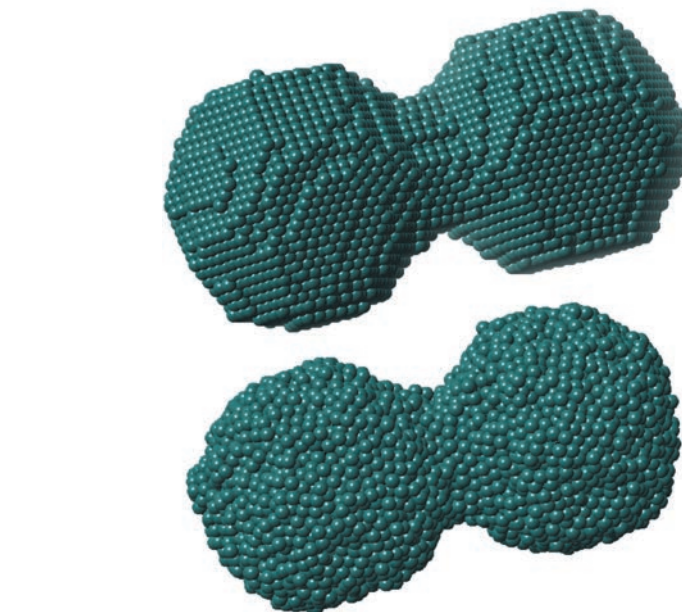
Metal nanoparticles with a disordered, glass-like structure coalesce faster than conventional metal nanoparticles that have a crystalline structure, experimentalists at the AIMR have discovered¹. This finding has significant implications for their use, since the properties of nanoparticles depend greatly on their size.

Metallic glass nanoparticles are attracting much interest because of their potential for use in a wide range of applications, including catalysis, biomedical materials and the strengthening of composite materials. Unlike conventional metal nanoparticles, which have a regular, crystalline structure, metallic glass nanoparticles have a disordered arrangement of atoms.

Due to their tiny size, all nanoparticles are inherently unstable and they often tend to merge with each other to reduce their surface energy — in much the same way that two small bubbles will coalesce to form a larger, more stable bubble. Known as coarsening, this mechanism has been extensively studied in conventional metal nanoparticles because it leads to degrading of their physical and chemical properties. But the coarsening mechanisms of metallic glass nanoparticles remain largely unknown.

“The coarsening mechanism is important for nanoparticles because it determines their sintering kinetics and their subsequent stability,” says Yuan Tian, who is the first author of the study.

Now, by using a state-of-the-art *in situ* heating transmission electron microscope that allowed them to observe nanoparticles coalesce stably at high temperatures, a team led by Mingwei Chen of the AIMR at Tohoku University has found that metallic glass nanoparticles



The disordered arrangement of atoms in metallic glass nanoparticles (bottom) allows two nanoparticles to merge faster than two conventional metal nanoparticles which have a crystalline structure (top).

coalesce much faster than their crystalline counterparts at temperatures of a few hundred degrees Celsius.

“This special coalescence behavior of metallic glass nanoparticles came as a surprise to us,” says Tian. “This new aspect of metallic glass nanoparticles is important for informing their future study.”

To gain more insight into the coarsening mechanism, the team also performed computer simulations of the nanoparticles. They found that the greater mobility of surface atoms and the isotropic structure of metallic glass nanoparticles are the main drivers of their faster coalescence compared to their conventional cousins (see image).

“During coalescence, metallic glass nanoparticles keep their round shape,

whereas crystalline nanoparticles gain sharp edges,” explains Tian. “The different morphologies of crystalline and amorphous nanoparticles give their surface atoms different mobilities, and this, in turn, gives rise to their different coarsening mechanisms.”

The team intends to investigate the coarsening process of larger metallic glass particles. “We plan to extend this study to larger scales because we anticipate that the coarsening mechanism will change when the particles are larger than about 10 micrometers,” says Tian.

1. Tian, Y., Jiao, W., Liu, P., Song, S., Lu, Z., Hirata, A. & Chen, M. Fast coalescence of metallic glass nanoparticles. *Nature Communications* **10**, 5249 (2019).

TOPOLOGICAL SUPERCONDUCTORS

Published online on 30 March 2020

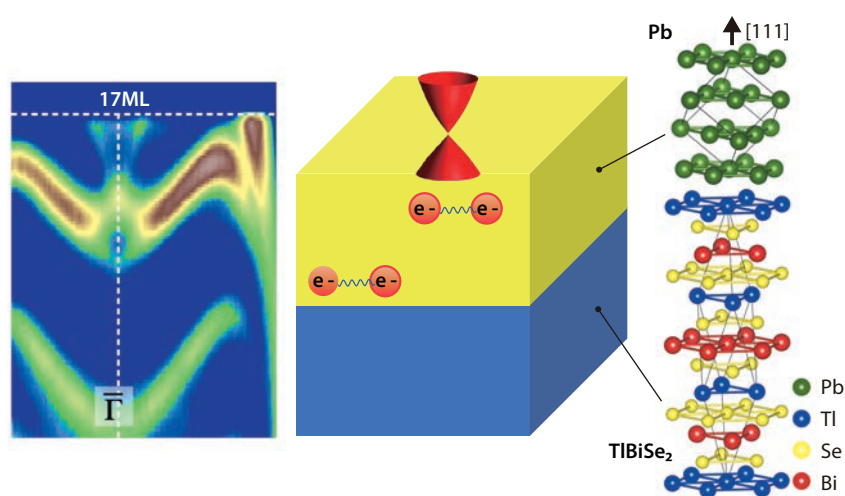
Turning a conventional superconductor into a topological one

A new method produces topological superconductors, which are attractive for quantum computing

A new way to make topological superconductors — promising materials for realizing robust quantum computers that are more tolerant of faults than existing technologies — has been discovered by AIMR researchers¹. This method should make it possible to convert conventional superconductors into topological ones, greatly increasing the number of topological superconducting systems.

Superconductors can conduct electricity without resistance. A special class known as topological superconductors are superconducting everywhere except on their surfaces, where they conduct electricity with a low resistance, like metals do. They are exciting interest because they could host exotic quasiparticles known as Majorana fermions. Named after the Italian physicist who predicted their existence about 80 years ago, Majorana fermions are attractive for realizing fault-tolerant quantum computers. While they have yet to be definitively observed, there is mounting experimental evidence for their existence.

Until now, topological superconductors have generally been made by bringing a superconductor into contact with a topological insulator — a material that is electrically insulating internally but conductive on its surface. The superconductor imparts a thin portion of the topological insulator with superconductivity, an effect known as the superconducting proximity effect. But it is hard to detect Majorana fermions in such topological superconductors. “Since the superconducting proximity effect occurs at an interface far from the surface, it is generally difficult to probe Majorana fermions by surface spectroscopy techniques,” explains Takafumi



Spectroscopic measurements (left) strongly suggest that a superconducting lead film (yellow layer in central image) on a topological insulator (blue layer) is a topological superconductor.

Sato of the AIMR at Tohoku University.

Sato and co-workers have produced a topological superconductor by reversing the influence between the superconductor and the topological insulator — they transferred topological properties to a conventional superconductor. They did this by growing a thin film of superconducting lead on a topological insulator, which proved to be quite challenging. “Until our study, no-one had ever succeeded in fabricating a lead film on a topological insulator,” says Sato. “It was a big challenge and we had to optimize the growth conditions very carefully and fabricate more than 70 samples until we got one that was satisfactory.”

The team then performed spectroscopy measurements that strongly suggested that they had produced a topological superconductor.

The team’s method opens up the possibility of producing topological superconductors in a much wider range of systems than before. “Our concept may be widely applicable to other combinations of superconductors and topological insulators,” says Sato. “Exploring new material systems based on our idea, could accelerate investigations of topological superconductors and the detection of Majorana fermions and ultimately, their possible applications to quantum computation.”

1. Trang, C. X., Shimamura, N., Nakayama, K., Souma, S., Sugawara, K., Watanabe, I., Yamauchi, K., Oguchi, T., Segawa, K., Takahashi, T. *et al.* Conversion of a conventional superconductor into a topological superconductor by topological proximity effect. *Nature Communications* **11**, 159 (2020).

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SUPERCONDUCTIVITY

Published online on 27 April 2020

Crystal geometry affects transition temperatures

Superconductivity can be induced in layered bismuth compounds by varying the geometry of their crystal structure

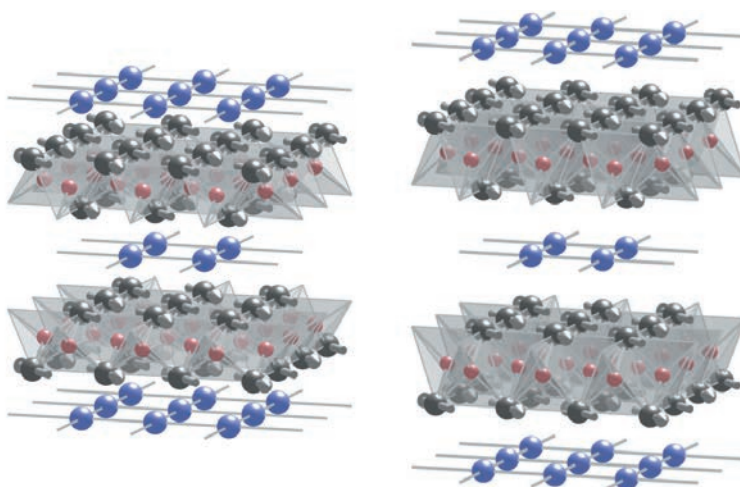
The temperature at which superconductivity begins in layered, bismuth-containing compounds can be increased by altering the geometry of its crystal structure, an AIMR-led team has discovered¹. This could open up a new way to manipulate superconductivity in layered materials and provide vital hints on the mechanism of superconductivity.

Some materials made up of alternating layers are superconductors, the best-known examples being cuprates and iron-based compounds. Although these compounds have been researched intensively, no one knows exactly how they superconduct.

These materials are usually made to superconduct by ‘doping’ them with elements that provide additional electrons. But a recent study has found that twisting a double layer of graphene can induce superconductivity, suggesting that geometric manipulation of crystal structure factors may be important.

Now, Tomoteru Fukumura of the AIMR at Tohoku University and his co-workers have found that compounds consisting of alternating layers of bismuth and of a rare-earth oxide superconduct. Furthermore, they discovered that the temperature for the onset of superconduction increases as the ratio of the distance between the bismuth layers to the distance between adjacent bismuth atoms in a layer increases, or, expressed another way, as the ratio of the lengths of the two sides of the unit cell increases.

The researchers varied this ratio in two ways: they made compounds containing five different rare-earth elements, which have different ionic sizes, and they added excess oxygen atoms to the compounds, effectively wedging the layers apart



An AIMR-led team has found that increasing the ratio of the distance between two bismuth layers and the distance between adjacent bismuth atoms (purple spheres) in a layer increases the temperature at which superconduction occurs. They varied this ratio by adding excess oxygen atoms (red spheres; see image on right) and using different rare-earth atoms (dark-gray spheres).

(see image). Interestingly, the temperature at which superconductivity starts depended only on the structural ratio — it did not depend on which rare-earth element was present or on the magnetic ordering in the rare-earth layer.

“We thought that the compound containing the rare-earth element dysprosium might not be superconducting because it has magnetic ordering, which usually destroys superconductivity,” explains Fukumura. “But even it became superconducting at about 2 kelvin on adding excess oxygen, just like nonmagnetic Y_2O_2Bi .”

“Layered compounds such as cuprates and iron-based compounds have generally been made to superconduct by carrier doping, but our layered compound becomes superconducting by increasing

the unit cell ratio, which is a purely crystallographic parameter,” says Fukumura. “It will be very interesting to see if this parameter induces superconductivity in other layered compounds.”

At this stage, the team is not sure why the ratio affects the superconducting transition temperature. To get more clues, they are investigating where the added oxygen ends up in the crystal structure. They are also looking for a way to vary the unit cell ratio that does not involve adding oxygen to the layered compound.

1. Sei, R., Kawasoko, H., Matsumoto, K., Arimitsu, M., Terakado, K., Oka, D., Fukuda, S., Kimura, N., Kasai, H., Nishibori, E. *et al.* Tetragonality induced superconductivity in anti-ThCr₂Si₂-type RE₂O₂Bi (RE = rare earth) with Bi square nets. *Dalton Transactions* **49**, 3321–3325 (2020).

LITHIUM–OXYGEN BATTERIES

Published online on 25 May 2020

Synergism between catalysts boosts efficiency

Using both solid and liquid catalysts enhances the energy efficiency of lithium–oxygen batteries

Solid and liquid catalysts in a lithium–oxygen rechargeable battery have a synergistic effect that simultaneously boosts the cathode kinetics and energy efficiency of the battery, researchers at the AIMR have found¹. This points the way to overcome two of the main hurdles to the commercialization of these batteries.

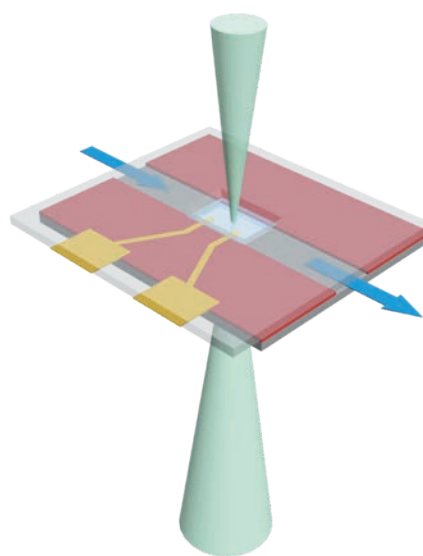
“The lithium–oxygen battery is one of the most promising candidates for the next generation of electrochemical energy-storage devices,” says Mingwei Chen of the AIMR at Tohoku University. “But its practical implementation has been hindered by sluggish kinetics at the cathode and low energy efficiencies.”

Lithium–oxygen batteries consist of three main components: a lithium metal anode, a non-aqueous liquid electrolyte and a porous cathode. During discharging, the battery releases energy through the oxidization of lithium to lithium peroxide (Li_2O_2), and it stores energy during charging by the reverse reaction in which lithium peroxide is decomposed into lithium and oxygen. Catalysts are needed to facilitate both these reactions.

Solid and liquid catalysts have been developed for lithium–oxygen batteries, but they both have their downsides. “Solid catalysts suffer from rigid and unstable catalyst–lithium peroxide interfacial contacts, whereas liquid catalysts have lower catalytic efficiencies,” explains Chen.

Previous studies had shown the promise of using both solid and liquid catalysts for improving the energy efficiency of lithium–oxygen batteries, but until now the underlying mechanisms and the optimal combinations have not been explored.

The team led by Chen used a state-of-the-art liquid-cell transmission electron



AIMR researchers used an electron beam (green cones) from a high-angle annular dark-field scanning transmission electron microscopy to image nanoscale interfacial electrochemical reactions in real space. The two blue arrows indicate the flow of an electrolyte containing the liquid catalyst tetrathiafulvalene, while the gold plates on the left are used to apply a potential across two gold electrodes.

microscope to investigate the effect of using both kinds of catalysts.

Chen and his team chose ruthenium oxide (RuO_2) as the solid catalyst and tetrathiafulvalene ($\text{C}_6\text{H}_4\text{S}_4$) as the liquid catalyst. They then imaged the dynamic nanoscale reactions that took place at the interfaces between the electrode and the electrolyte, and between the electrode and the lithium peroxide (see image).

The researchers discovered a synergistic effect between the two catalysts — in addition to catalyzing lithium–oxygen reactions, the solid catalyst enhanced the catalytic efficiency of the liquid catalyst during discharging. The liquid catalyst activated the lithium

peroxide–passivated ruthenium oxide and accelerated the oxidation of lithium peroxide during charging. This synergistic effect boosted the energy efficiency of the rechargeable lithium–oxygen battery.

Chen and his team plan to build upon this work. “Using the electrochemistry insights gained in this study, we intend to work toward developing better combinations of solid and liquid catalysts for high-performance lithium–oxygen batteries,” says Chen.

1. Hou, C., Han, J., Liu, P., Huang, G. & Chen, M. Synergetic effect of liquid and solid catalysts on the energy efficiency of Li–O₂ batteries: cell performances and operando STEM observations. *Nano Letters* **20**, 2183–2190 (2020).

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MAGNONS

Published online on 29 June 2020

Sophisticated amplification process underpinned by simple math

An advance that may help to realize a futuristic form of computing can be described by the same equations as for a child playing on a swing

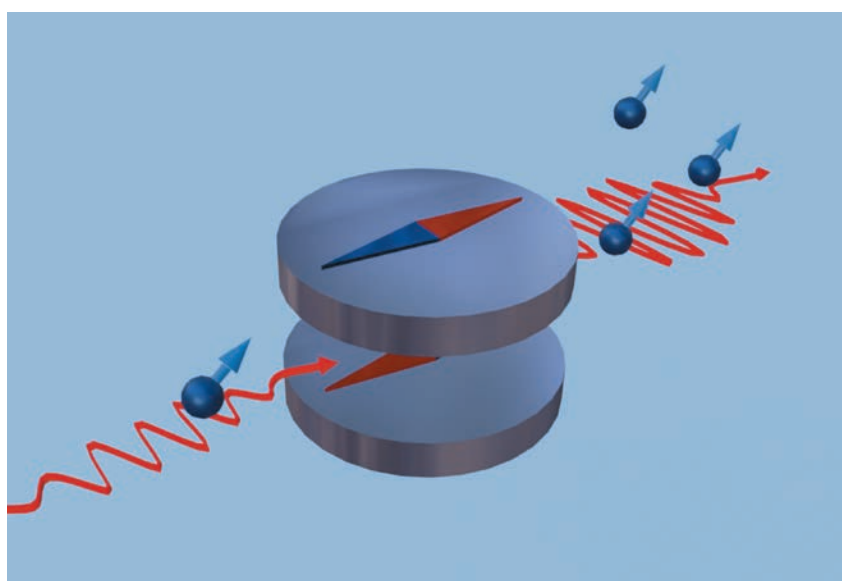
A convenient way to amplify wave-like precessions of electron spin in a magnetic material with a sandwich-like structure has been found by AIMR researchers¹. This amplification could find use in a new generation of computers inspired by the brain.

Conventional, silicon-based computer technology is rapidly approaching the physical limits of miniaturization. As a result, engineers are searching for alternative computing technologies for the ‘post-silicon era’. One promising technology is neuromorphic computing, which seeks to mimic how the brain processes data.

Precessions of electron spins known as magnons, which can exhibit both particle-like and wave-like behaviors, are attractive candidates for use as information carriers in neuromorphic computers. But because magnons cannot sustain themselves, an energy-efficient, nanoscale way to amplify them is needed before they can be used in circuits.

Previously, Shigemi Mizukami of the AIMR at Tohoku University and co-workers had observed two modes of magnons in a synthetic antiferromagnet — a magnetic material that consists of a non-magnetic layer sandwiched between two ferromagnetic layers, where the magnetizations of the ferromagnetic layers point in opposite directions. They saw a high-frequency optical mode and a low-frequency acoustic mode.

Now, by using a technique they developed that employs ultrafast laser pulses, Mizukami and his colleagues have found that the optical magnon mode amplifies the acoustic mode when they interact (see image). Specifically, they found that



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AIMR researchers have found a way to amplify magnons (blue spheres with arrows indicating spin) in a synthetic antiferromagnet consisting of two ferromagnetic layers (horizontal circles) sandwiched between a non-magnetic material.

the acoustic mode gets a temporary kick from the optical mode when its frequency is roughly half that of the optical mode.

The researchers anticipate that this effect could be used to produce an energy-efficient nanoamplifier of magnons. “This finding is a first and important step towards realizing magnonic computing,” says Mizukami. “In particular, it gives a new perspective for developing nanoscale spintronic elements that will form the building blocks for future neuromorphic computers.”

To gain more insights into the effect, the researchers performed a mathematical analysis of the magnon amplification. To their surprise, they found that the equations describing the phenomenon

are the same as those for a child propelling a swing by moving their legs. “The math underpinning this effect is identical to that for a child on a swing,” says Mizukami. “The math is very simple and describes many physical phenomena in nature, but we were surprised to discover that such fundamental physics is inherent in a synthetic antiferromagnet.”

The researchers intend to realize new magnonic computing architectures utilizing this amplification principle in synthetic antiferromagnets.

1. Kamimaki, A., Iihama, S., Suzuki, K. Z., Yoshinaga, N. & Mizukami, S. Parametric amplification of magnons in synthetic antiferromagnets. *Physical Review Applied* **13**, 044036 (2020).

Droplets hanging from a liquid surface

A curious effect observed during an experiment could find application in microrobots

A way to suspend droplets of a denser fluid from the surface of a less dense fluid has been found by an international team led by an AIMR researcher¹. This unusual effect could find application in microreactors and microrobots.

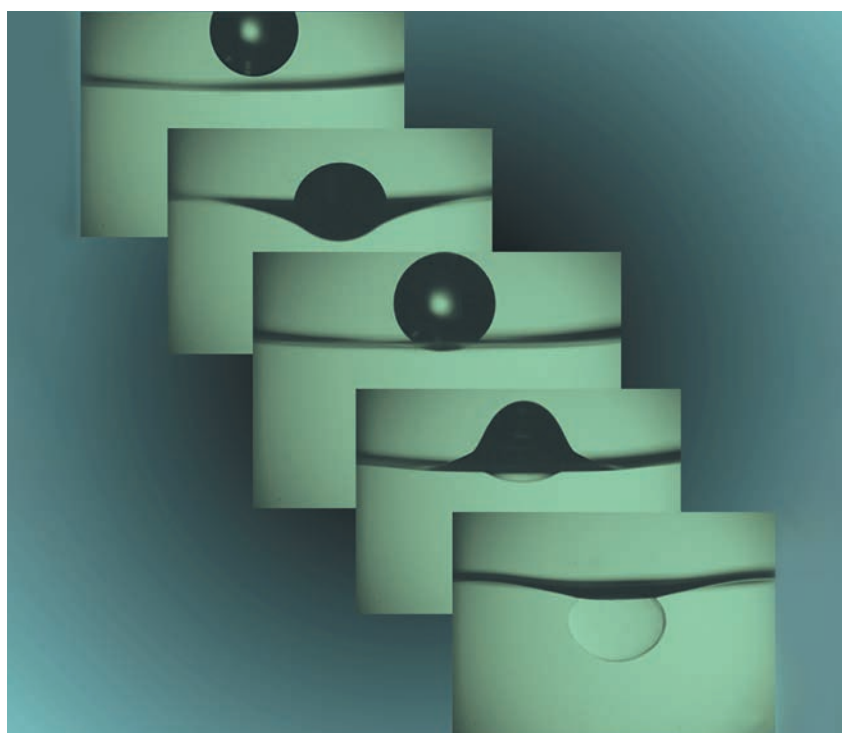
If you drop a liquid such as water into a less dense, immiscible liquid such as oil, it will sink to the bottom of the container. But a team led by Thomas Russell of the AIMR at Tohoku University noticed something curious while they were investigating the printing of three-dimensional water structures in water in a previous study—they found that some water droplets containing a polycation and dextran (a polysaccharide made up of many glucose molecules) hung from the surface of aqueous solutions of the polymer poly(ethylene glycol) (PEG) with a polyanion.

What made it more puzzling was the fact that the two solutions have an extremely low interfacial tension—the attractive force between molecules across the interface of two fluids. Some insects exploit the high interfacial energy between their highly water repellent legs and water to walk on water, but the interfacial energy is very low in the case of dextran and PEG.

“This effect was unexpected,” says Russell. “It was very curious how the heavier droplet could hang on the liquid surface with such a low interfacial tension.”

With their curiosity piqued, Russell and his co-workers looked deeper into the effect. They discovered that a polyelectrolyte complex formed at the interface between two aqueous solutions and that this allowed the heavier dextran droplets to hang from the PEG surface.

“The condition for hanging the dextran droplet from the interface between



© 2020 Thomas Russell

Dropping a droplet of dextran (top frame) onto the surface of an aqueous solution of poly(ethylene glycol) (PEG) causes it to be suspended from the PEG surface (bottom frame). Although dextran is denser than PEG, a polyelectrolyte complex enables it to hang from the surface.

air and PEG is determined solely by the force balance between gravitational stresses and surface stresses on the PEG side of the droplet,” explains Russell. “Remarkably, nothing else matters.”

The droplets are highly versatile, making them promising for use in microrobots and microreactors. “By embedding magnetic microparticles in the hanging droplets, we could get them to move and rotate under the influence of an applied magnetic field,” says Russell. “Also, we found a hanging droplet with an opening to air could, like a mosquito larva, use air

to perform some reactions and induce a cascade reaction in a neighboring droplet.”

The team is now creating a bioinspired meniscus-climbing system, which can transport and shuttle materials from the land to the solution on the liquid surface. They also have plans to use the system to create an artificial cell that can fix carbon dioxide.

1. Xie, G., Forth, J., Zhu, S., Helms, B. A., Ashby, P. D., Shum, H. C. & Russell, T. P. Hanging droplets from liquid surfaces. *Proceedings of the National Academy of Sciences USA* **117**, 8360–8365 (2020).

Record-high lithium-ion conductivity at room temperature

Lightweight rotating structures in hydride complexes are promising for developing solid-state electrolytes

Researchers at the AIMR have hit upon a way to get polyanions to rotate at much lower temperatures than normal, opening the possibility of realizing solid-state batteries with short charging times¹.

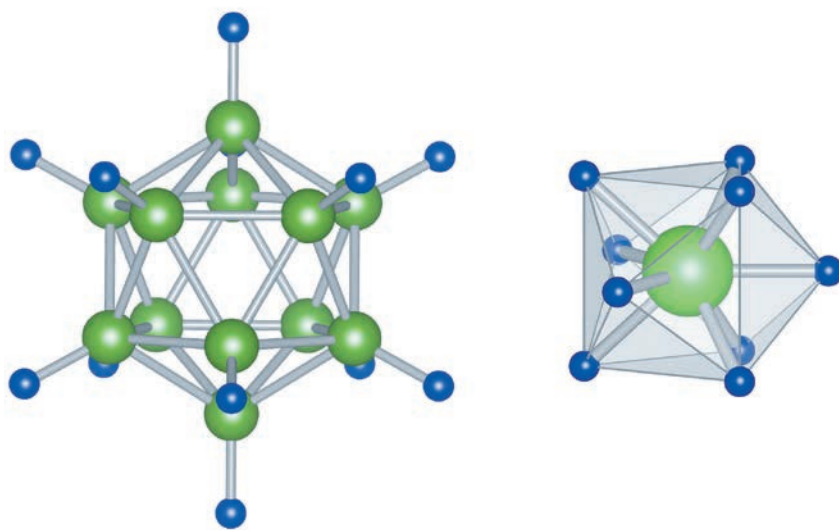
Most commercial batteries use liquid electrolytes to convey charges between their electrodes, but if solid electrolytes could be used instead, batteries would be both safer and able to store more energy at the same volume.

Solid-state batteries require solid electrolytes that have high conductivities for ions. One promising class of material for realizing this is ionic conductors that contain polyanions — ions that have multiple negatively charged groups. The polyanions rotate at high temperatures, and this motion assists the conduction of positive ions through the material. But this rotation, and hence the high ion conductivity, does not occur at room temperature, making it impractical for many applications.

Now, four researchers at Tohoku University, including two from the AIMR, have realized a room-temperature lithium-ion conductivity in a hydride that is more than three times higher than the highest value obtained to date.

The results exceeded the team's expectations. "We were surprised since the activation energy for rotation was lower than we had expected," says Shigeyuki Takagi of the Institute for Materials Research at Tohoku University. "We anticipate that our finding will promote the development of rechargeable batteries with very short charging times."

Previous studies had used bulky anions as the rotating elements, which require significant activation energies to get them to rotate. In contrast, Takagi and his team



Typical rotatable polyanions, such as $B_{12}H_{12}^{3-}$ (left), are bulky and thus require a large activation energy to get them to rotate. In contrast, the pseudorotation of MoH^{3-} (right) only involves the rotation of hydrogen atoms (blue spheres) and hence the polyanion can rotate even at room temperature.

achieved the high lithium-ion conductivity at room temperature by using the transition metal molybdenum surrounded by nine hydrogen atoms. Because the rotating components are lightweight hydrogen atoms, the rotation occurs even at room temperature (see image).

The rotation of the hydrogen atoms is actually not a true rotation, but a pseudorotation involving just small displacements of the hydrogen atoms. This further promotes the lowering of the activation energy.

"The pseudorotation enhances the dynamic disorder of the hydrogen atoms, thereby increasing the entropy, which thermodynamically stabilizes the pseudorotating high-temperature phase at low temperature," says Takagi.

The researchers anticipate that the same strategy should be applicable to other polyanionic materials. "Because the mechanism is quite general, we think that it should be useful for developing all-solid-state secondary batteries with different carriers, such as sodium and magnesium ions," notes Takagi.

The team is now planning to experimentally demonstrate room-temperature superionic conduction, which has been predicted theoretically.

1. Takagi, S., Ikeshoji, T., Sato, T. & Orimo, S. Pseudorotating hydride complexes with high hydrogen coordination: A class of rotatable polyanions in solid matter. *Applied Physics Letters* **116**, 173901 (2020).

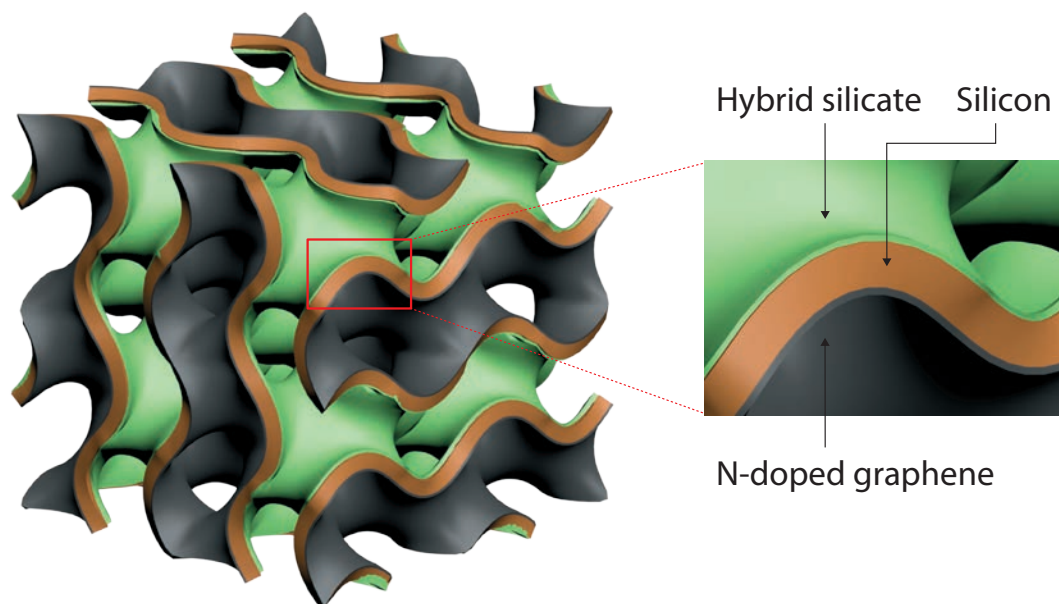
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LITHIUM-ION BATTERIES

Published online on 28 September 2020

Making silicon usable

Anodes with specially designed nanoarchitectures beat the limitations of silicon anodes



The structure of the nanoporous silicon anode produced by AIMR researchers. One side of the silicon is coated with hybrid silicate, while the other side is coated with nitrogen-doped graphene.

Hybrid silicon anodes for lithium-ion batteries that overcome problems that had previously beset silicon anodes have been created by AIMR researchers¹. This advance will help increase the energy storage of next-generation lithium-ion batteries.

Lithium-ion batteries are ubiquitous today, being used to power everything from smart phones to electric vehicles. However, the graphite-based anodes used in today's batteries are approaching the limit of their development, and a new anode material is needed to realize lithium-ion batteries with even higher energy capacities.

Silicon is a promising alternative anode material because it is cheap and abundant and has a large reversible capacity and a good working potential. "Exploiting these advantages of silicon will result in a further breakthrough in the energy density of lithium-ion batteries," predicts Mingwei Chen of the AIMR at Tohoku University.

But silicon suffers from three significant problems. One is that it expands

and contracts a lot during charging and discharging, changing its volume by more than a factor of three. This degrades the electrodes and can result in loss of electrical contact inside the battery. Another problem with silicon is its low conductivity, which reduces the charging and discharging rate. A third problem is that the protective film that forms between silicon and the electrolyte during the first few charging cycles is unstable.

Now, the team led by Chen has overcome all these problems by designing and producing a nanoporous silicon anode that has a sandwich-like structure. In this anode, the silicon is coated on one surface by nitrogen-doped graphene and on the other surface by a hybrid silicate (see image).

Both surfaces play important roles in overcoming the above-mentioned limitations of silicon. "The nanoporous graphene in the anode acts as a flexible and conductive backbone that

simultaneously accommodates silicon's volume change and improves its electrical conductivity," explains Chen. "On the other hand, the hybrid silicate coating acts as a protective outer shell, enhancing the robustness and suppleness of the electrode and facilitating the formation of stable films on the anode surface."

In tests involving half and full cells, the anode exceeded the team's expectations, realizing both an excellent cycling performance and rate capability. "We were really surprised by the ultrahigh stability of this hybrid silicon anode," says Chen. "It was stable over 10,000 cycles and had a high capacity and ultrahigh charging rate."

The team now plans to stack several free-standing graphene-silicon sheets to boost the energy storage capacity.

1. Huang, G., Han, J., Lu, Z., Wei, D., Kashani, H., Watanabe, K. & Chen, M. Ultrastable silicon anode by three-dimensional nanoarchitecture design. *ACS Nano* **14**, 4374–4382 (2020).

Metal–insulator transition observed in nanowires

Nanowires of a transition metal oxide switch from metallic to insulating with decreasing width

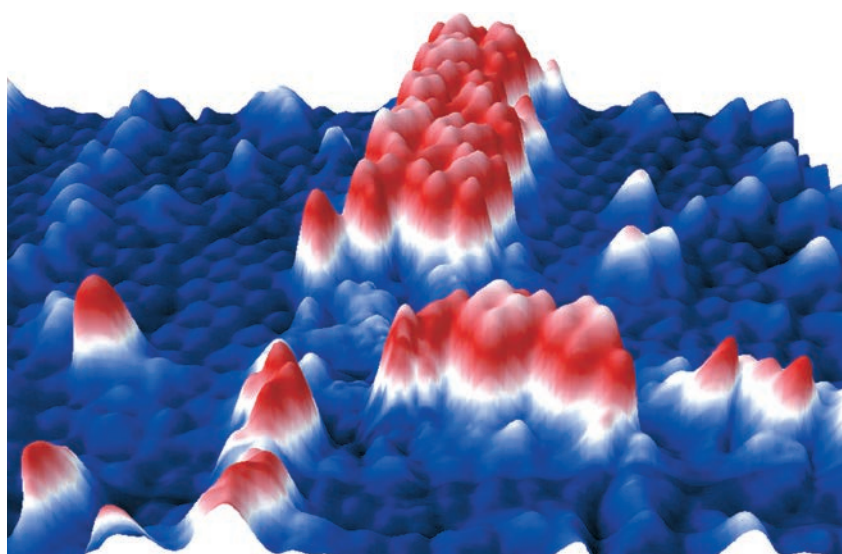
The electronic states of nanowires of a transition metal oxide go from being metallic to insulating on reducing the nanowire width, a team of AIMR researchers has shown¹. In the future, such a metal–insulator transition could find application in phase-change memory devices and sensors.

Physicists find transition metal oxides fascinating systems to experiment with because their electrons interact strongly with each other, giving rise to a range of exotic effects such as high-temperature superconductivity and colossal magnetoresistance.

One-dimensional nanowires of transition metal oxides are expected to harbor even more interesting phenomena because their electronic states are subject to strong quantum fluctuations. Three-dimensional crystals and two-dimensional ultrathin films of transition metal oxides have been extensively studied, but it is difficult to fabricate one-dimensional nanowires using conventional nanofabrication techniques because of their relatively complex crystal structures.

Now, Hirofumi Oka of the AIMR at Tohoku University and his co-workers have succeeded in spontaneously forming nanowires of the transition metal oxide strontium vanadate (SrVO₃) for the first time.

The team found that the electronic states of the nanowires depended strongly on the nanowire width, going from metallic to insulating as the nanowires got narrower. This finding mirrors what is observed in ultrathin films of strontium vanadate, which undergo a metal–insulator transition with decreasing thickness. While the mechanism has yet to be



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A three-dimensional image generated from a topographic scanning tunneling microscope image of strontium vanadate nanowires formed on an ultrathin film of strontium vanadate.

definitively determined, the researchers speculate that the electronic states in the nanowire may be quantized due to the quantum confinement caused by the low dimensionality of the nanowires.

The team used pulsed laser deposition to form the nanowires on the surface of a strontium vanadate ultrathin film (see image). This was unexpected, and the mechanism is currently being explored. “The spontaneous formation of one-dimensional strontium vanadate nanowires was very surprising,” notes Oka. “Despite the simple cubic perovskite structure of strontium vanadate, the crystal grows in only one direction.”

The state-of-the-art equipment at the AIMR was crucial for producing the nanowires. “The fabrication of the strontium vanadate nanowires was due in large

part to our world-class low-temperature scanning tunneling microscope combined with pulsed laser deposition,” notes Oka. “This system allowed us to characterize the atomic structure *in situ*.”

In the future, the team intends to see if they can induce superconductivity in the nanowires. “It will be interesting to see if insulating strontium vanadate nanowires become superconducting on carrier doping because one-dimensional superconductors are expected to exhibit high-temperature superconductivity due to strong quantum fluctuations,” says Oka.

1. Oka, H., Okada, Y., Kaminaga, K., Oka, D., Hitosugi, T. & Fukumura, T. Width-induced metal–insulator transition in SrVO₃ lateral nanowires spontaneously formed on the ultrathin film. *Applied Physics Letters* **117**, 051603 (2020).

TOPOLOGICAL INSULATORS

Published online on 30 November 2020

Filling in the knowledge gaps

A new approach succeeds in inducing a Dirac gap in a topological insulator, bringing the potential for exotic quantum effects

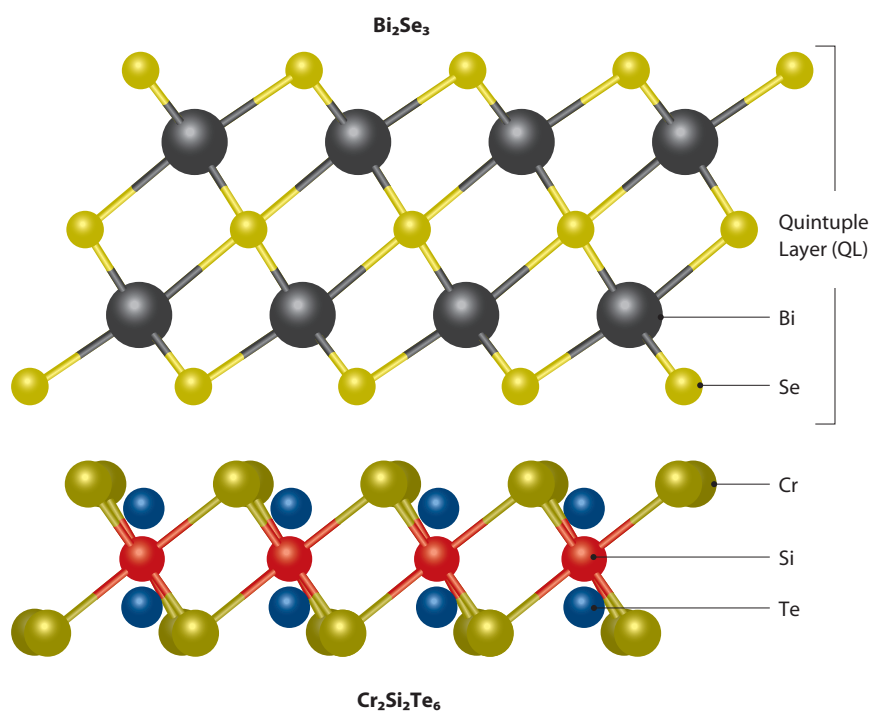
Growing a material known as a topological insulator on a ferromagnet could open the way to create various exotic quantum effects in the topological insulator, AIMR researchers have shown¹. This structure could be used in spintronic applications for converting between spin and charge currents.

Topological insulators have generated a huge amount of interest since their discovery in 2007. Their most well-known property is their ability to conduct electricity along their surfaces while being electrically insulating inside.

Although topological insulators are interesting in their own right and promising for applications in the area of spintronics, even more exotic quantum effects could be induced in them if were possible to create an energy gap known as the Dirac gap. One way to do this is to introduce magnetic impurities into a topological insulator, but this creates defects in the material and can be used only at low temperatures.

Now, Takafumi Sato of the AIMR at Tohoku University and his co-workers have demonstrated a new strategy to create a Dirac gap in a topological insulator. They grew ultrathin films of a topological insulator on a ferromagnet and observed a Dirac gap when the topological insulator was about 2 nanometers thick (see image).

This Dirac gap was induced by an effect known as interfacial coupling, whereby the ferromagnetism of the magnetic layer influences the electron states on the surface of the topological insulator. “Our result suggests that interfacial coupling, which had not been considered much in previous studies, is crucial for controlling Dirac fermions in heterostructure systems involving a topological insulator,” says Sato. “This will help toward



AIMR researchers have induced a Dirac gap in a topological insulator by growing an ultrathin film of the topological insulator Bi_2Se_3 on the ferromagnet $\text{Cr}_2\text{Si}_2\text{Te}_6$.

realizing exotic topological phenomena and device applications of topological insulators.”

The team hadn’t expected the effect to be so strong. “Before doing the experiment, we thought that interfacial coupling would modulate the Dirac cone only by a very small amount,” says Sato. “However, to our surprise, the interfacial coupling turned out to alter the overall band dispersion of the Dirac-cone surface states when the topological insulator film was thin enough.”

Fabricating high-quality topological insulator thin films on the ferromagnet was challenging, but the team succeeded thanks to state-of-the-art techniques and

helpful collaborators. “Critical to our successful film growth was a sophisticated molecular-beam-epitaxy technique developed in our laboratory and high-quality single crystals provided by Eiji Saitoh’s team,” says Sato.

The team now intends to explore different combinations of topological insulators and ferromagnets in order to enhance the ferromagnetic proximity.

1. Kato, T., Sugawara, K., Ito, N., Yamauchi, K., Sato, T., Oguchi, T., Takahashi, T., Shiomi, Y., Saitoh, E. & Sato, T. Modulation of Dirac electrons in epitaxial Bi_2Se_3 ultrathin films on van der Waals ferromagnet $\text{Cr}_2\text{Si}_2\text{Te}_6$. *Physical Review Materials* **4**, 084202 (2020).

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THERMOELECTRIC MATERIALS

Published online on 21 December 2020

Porous structure captures heat more efficiently

Honeycomb-like material hits the sweet spot for harvesting waste heat

An ultralight material developed by AIMR researchers that can absorb waste heat and convert it directly into electricity could significantly enhance the energy efficiencies of vehicles and power plants¹.

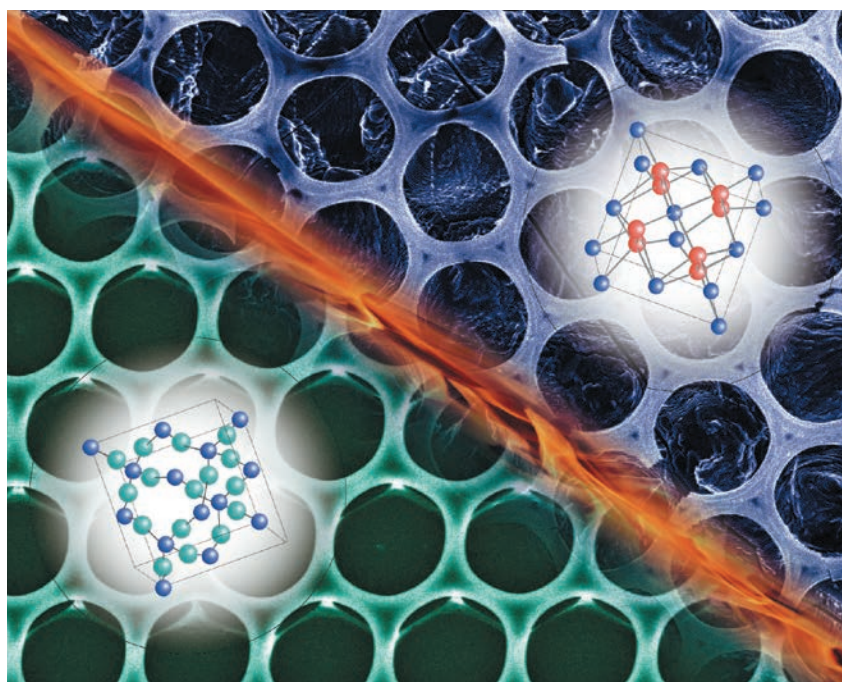
When one side of a thermoelectric material is heated, the resulting temperature gradient generates a voltage across the material. In principle, these materials should be ideal for recapturing the large amounts of energy lost as waste heat by many machines and devices. “The exhaust heat emitted from engines of automobiles and turbines of power plants is huge, and as much as 60% of it is lost to the environment,” says Hiroshi Yabu of the AIMR at Tohoku University.

However, although many thermoelectric materials are known, few operate with high efficiency in the 125–625 degrees Celsius temperature range that corresponds to the flow of exhaust heat from vehicles, gas turbines and other industrial processes.

Magnesium silicide is an exception. “Magnesium silicide is one of the few thermoelectric materials composed of Earth-abundant elements and that exhibits an optimum temperature near 425 degrees Celsius, which almost perfectly matches the temperature of industrial waste heat,” says Yabu.

A good thermoelectric material must have a high electrical conductivity, but it should also have a low thermal conductivity to ensure that its cold side stays cold and the temperature gradient is maintained.

Since magnesium silicide’s thermal conductivity is too high for practical use, Yabu and his colleagues have been developing ways to slow heat transfer through the material. “The introduction of a porous structure is an effective approach to reduce the thermal conductivity, but conventional techniques to fabricate porous magnesium silicide also reduce



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Treatment with magnesium vapor at 725 degrees Celsius converts a porous silica structure (bottom left, where the green spheres are oxygen atoms and the blue spheres are silicon atoms) into a high-performance thermoelectric material (top right, where the orange spheres are magnesium atoms and the blue spheres are silicon atoms).

its electrical conductivity due to defects forming,” he says.

Yabu’s team has now come up with a method to produce magnesium silicide with a honeycomb-like structure, introducing pores into the material but not defects. The researchers had previously developed a way to make a polymer honeycomb structure — in which the pores in the polymer were templated by water droplets — and to coat this structure with silica. They have now shown that silica can be converted into magnesium silicide honeycomb by treating silica-coated honeycomb with magnesium vapor at temperatures above 725 degrees Celsius (see image).

The resulting material was so light that it floated on water — an advantage

for weight-critical applications such as heat harvesting on vehicles. Critically, its thermal conductivity was 11% lower than that of bulk magnesium silicide, while its electrical conductivity did not change. “This result means that magnesium silicide honeycomb is a near-ideal thermoelectric material — it is ultralight, is made from abundant materials, and has a high thermoelectric conversion efficiency,” Yabu says.

1. Yabu, H., Matsuo, Y., Yamada, T., Maeda, H. & Matsui, J. Highly porous magnesium silicide honeycombs prepared by magnesium vapor annealing of silica-coated polymer honeycomb films toward ultralightweight thermoelectric materials. *Chemistry of Materials* **32**, 10176–10183 (2020).



AIMResearch

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