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Advanced Institute for Materials Research

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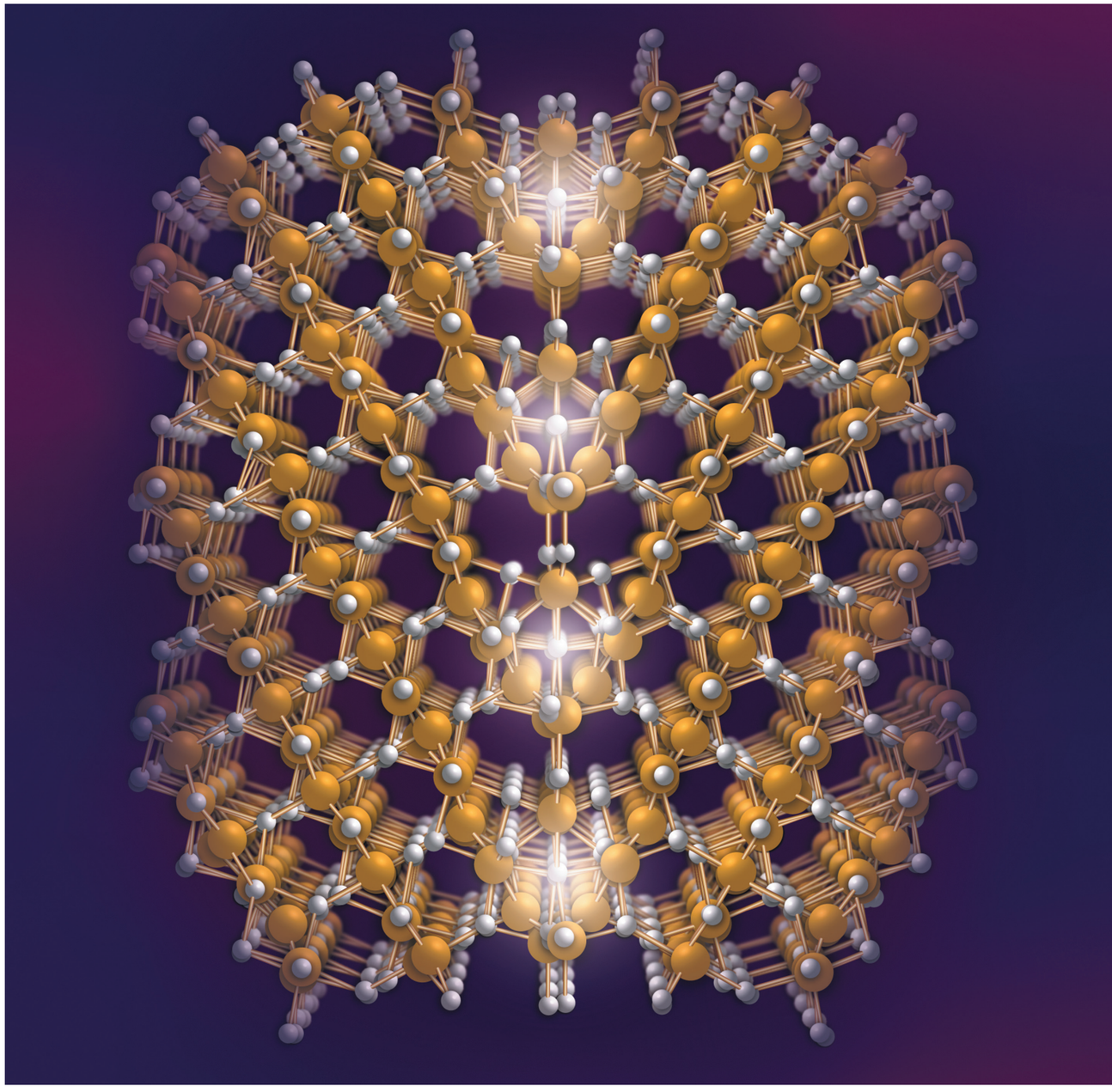
AiM Research

RESEARCH HIGHLIGHTS 2021

A publication of the WPI Advanced Institute for Materials Research



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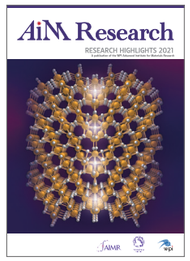

COVER STORY

Anatase-like grain boundary structure in rutile titanium dioxide predicted by ab initio random structure searching algorithm (See page 9).

COVER IMAGE

Design by Kazutoshi Inoue, Yuichi Ikuhara and Chris J. Pickard.
Illustration by ETOKAKU Co., Ltd.

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 (GI^3 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 29 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.

AIMR

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MESSAGE FROM THE DIRECTOR

Steadily advancing research and development in the midst of the coronavirus pandemic

The Advanced Institute for Materials Research (AIMR) in October 2022 marks 15 years since its founding. On this occasion, I would like to offer my heartfelt thanks to all of you who have made this possible through your support.

AIMR was launched in 2007 as one of the centers established by the World Premier International Research Center Initiative (WPI), a Japanese government project. Since that time, it has been continually engaged in new system creation and research and development activities on the way to becoming a global center for materials science. In this process, we have sought to carry out the WPI's four basic objectives, namely, advancing leading-edge research, creating interdisciplinary domains, establishing international research environments, and reforming research organizations. In 2012, AIMR began collaboration between mathematics and materials science, seeking to formulate new scientific principles that will enable the development of materials through prediction. It further develops devices and systems for putting to use in society the developed leading-edge materials, seeing as its mission helping to solve problems faced by humankind in such areas as resources and the environment.

In 2017, AIMR was recognized as a member of the WPI Academy, established to accelerate and expand global brain circulation. We intend to continue carrying out research at the top level worldwide, as a hub for global brain circulation.

A major feature of AIMR, the global center for materials science, is the above-noted collaboration between mathematics and materials science. By using the universal language of mathematics to describe materials science, which covers an extremely broad range, we aim to discover commonalities of various materials, and to pursue new topics to produce novel research results.

Dealing with the spread of the COVID-19 pandemic from around March 2020 has forced us to place certain limits on how research activities are carried out. Yet even as the pandemic has become protracted, AIMR, while taking every measure to control the spread of infections, has been steadily developing new principles and creating new materials. This work is proceeding mainly in three advanced target projects putting into practice mathematics-materials science collaboration, namely, 1) Local Structure Control in Topological Functional Materials, 2) Integrated Control of Bond Variation and its Time Evolution, and 3) Improvement of Self-Organization Technology and Control of Biological Response.

To give further momentum to these projects, along with awareness of the AIMR's strength of bringing researchers from different disciplines under one roof, I would like to call attention to the three Rs I have proposed as a way of maximizing this strength. The first R, Relief, refers to our guiding principle of not only giving priority to the safety and welfare of everyone involved in AIMR, but also giving importance to support of their mental wellbeing. The second R, Research, means the mental preparedness for continuing to run at the forefront of research, aware that in being at the leading edge of our research field we are at the same time at the "edge" in the sense of precipice. The third R, Recognition, means actively publicizing research results, so that the necessity of AIMR will be recognized more than ever in Japan and abroad.

With the help of all those who support AIMR, as we overcome the difficulties posed by the ongoing pandemic, I would like us to give substance to our mission of "bringing advanced materials science to the world." Along with becoming a core institute for building the global research environment of Tohoku University, we would like AIMR to contribute to the world's advanced materials science and to society.

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.

THREE-DIMENSIONAL GRAPHENE

Published online on 25 January 2021

Amping up graphene by bending it

The electronic states of 3D graphene are unaffected even by high curvatures

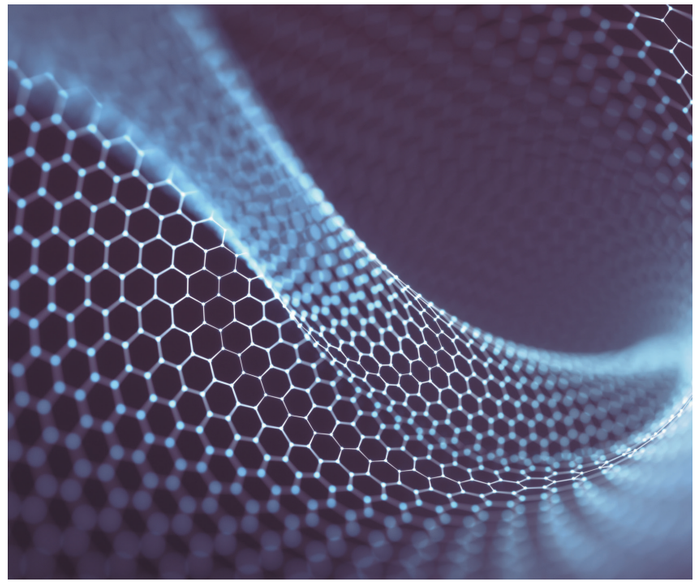
Bending graphene on a nanoscale maintains some of the excellent electrical properties of flat graphene while giving others a boost, an AIMR-led team has shown[1]. By providing engineers with another parameter to work with—namely the radius of curvature—this discovery could lead to novel devices based on three-dimensional (3D) graphene.

Graphene, a one-atom-thick honeycomb array of carbon atoms, exhibits many desirable properties (e.g., high electrical and thermal conductivities and high electron mobility), making it attractive for a wide range of applications. However, graphene's sheet-like structure is a problem because large areas are needed for devices, challenging compact-device fabrication.

One approach to this problem is to bend graphene into 3D nanostructures, packing large areas of graphene into tiny volumes. However, packing often deteriorates the properties of graphene by introducing defects and by disrupting the crystalline structure. Until now, what role, if any, the radius of curvature plays in this deterioration remains unclear.

Here, a team led by Mingwei Chen from AIMR fabricates bimodal porous graphene sponges with pore sizes ranging from 25 to 1,000 nanometers, and systematically investigates how the properties of graphene are affected by the radius of curvature.

The researchers discover that curvature does not alter the electronic states of graphene. Importantly, it preserves the Dirac fermion nature of electrons from which many of graphene's properties spring. "We showed that graphene with a radius of curvature between 50 and 1,000 nanometers maintained its Dirac fermion character," says Yoichi Tanabe, the first author of the study.



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Mingwei Chen's team has shown that the radius of curvature could provide engineers with an additional parameter when making devices based on curved graphene.

Furthermore, the team has found that the curvature can be used to tune the electrical transport properties of graphene. "We expect that the properties of graphene can be amplified by nearly 1,000 times in our 3D graphene sponge," says Tanabe.

Future directions will explore what effect varying the curvature-induced pseudo-magnetic field has on graphene. "We found that the pseudo-magnetic field acts a control parameter for curved surfaces of graphene," says Tanabe. "So next we will try controlling the physical properties unique to 3D curved surfaces by tuning this field."

1. Tanabe, Y., Ito, Y., Sugawara, K., Koshino, M., Kimura, S., Naito, T., Johnson, I., Takahashi, T. & Chen, M. Dirac fermion kinetics in 3D curved graphene. *Advanced Materials* **32,** 2005838 (2020).

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GRAIN-BOUNDARY STRUCTURE

Published online on 22 February 2021

Resolving atomic structure into polyhedra

The arrangement of atoms near the interface between two crystals can be represented in terms of polyhedra

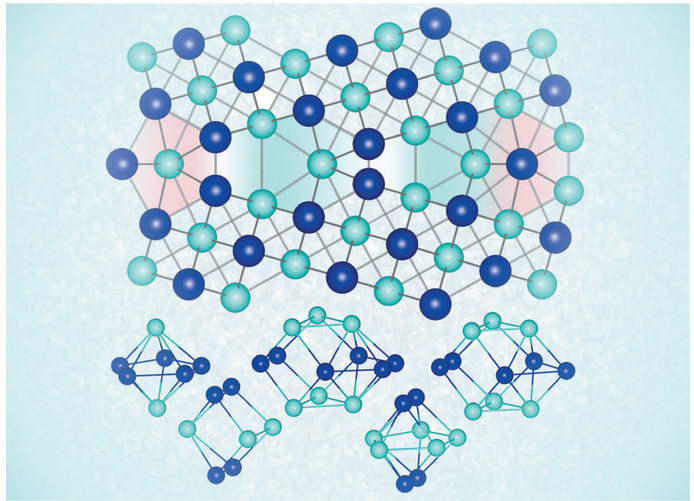
The atomic structures of regions near grain boundaries in polycrystalline materials can be characterized by certain types of polyhedra, AIMR researchers have shown[1]. This promises to make it easier to model these materials and to predict their properties.

Most metals and ceramics are three-dimensional (3D) mosaics of microscopic crystals of different sizes and orientations. The properties of such polycrystalline materials are strongly affected by how the atoms are arranged near the grain boundaries where two crystals meet. However, the breakdown of the regular structural order near these grain boundaries makes the structure-property relationship challenging to investigate.

For example, a crystal with a face-centered cubic (fcc) structure (e.g., aluminum, copper, and gold) can be considered to be made up of adjacent four-sided (tetrahedra) or eight-sided (octahedra) shapes.

Now, Kazutoshi Inoue of AIMR at Tohoku University and his co-workers have shown that it is also possible to analyze regions near grain boundaries in terms of atomic polyhedra (see Figure). They did this by analyzing the 3D polyhedral structure of fcc crystals for certain types of grain boundaries.

"We discovered that regions close to grain boundaries can be packed only by the bulk polyhedral units (i.e., tetrahedra and octahedra) or grain-boundary-type polyhedral units that differ from the bulk ones," says Inoue. "This extends the current two-dimensional model framework to define 3D polyhedral units, covering all the grain boundaries in cubic crystals."



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AIMR researchers have shown how the atomic structure near grain boundaries in certain polycrystalline materials (top structure) can be represented in terms of polyhedra (bottom structures).

The researchers also uncovered an unexpected connection between the grain-boundary atomic structures and the properties of fractions that can be represented by mathematical figures known as Farey diagrams.

"We found a one-to-one correspondence between the 3D atomic structures of grain boundaries and the distribution of rational numbers," says Inoue. "It's surprising that the grain-boundary hierarchy can be accurately described by a modified version of the Farey diagram, which also represents the mathematical structures of other physical and biological phenomena, including oscillations and phyllotaxy." This connection will enable researchers to readily estimate the 3D arrangement of grain boundaries.

The team intends to use this method in conjunction with microscopic observations to determine the conditions for realizing stable atomic structures at grain boundaries.

1. Inoue, K., Kawahara, K., Saito, M., Kotani, M. & Ikuhara, Y. 3D arrangement of atomic polyhedra in tilt grain boundaries. *Acta Materialia* **202,** 266–276 (2021).

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MAGNETO-OPTICS

Published online on 29 March 2021

Helical light creates spin at interfaces

A new way to generate electron spin using light could lead to ultrafast memory devices with low power consumption

Helical light beams can induce electron spins at the interface of a magnetic and non-magnetic material, three AIMR researchers have discovered[1]. This effect could form the basis of light-driven magnetic memory devices that are much faster and have far lower power consumption than present memory devices.

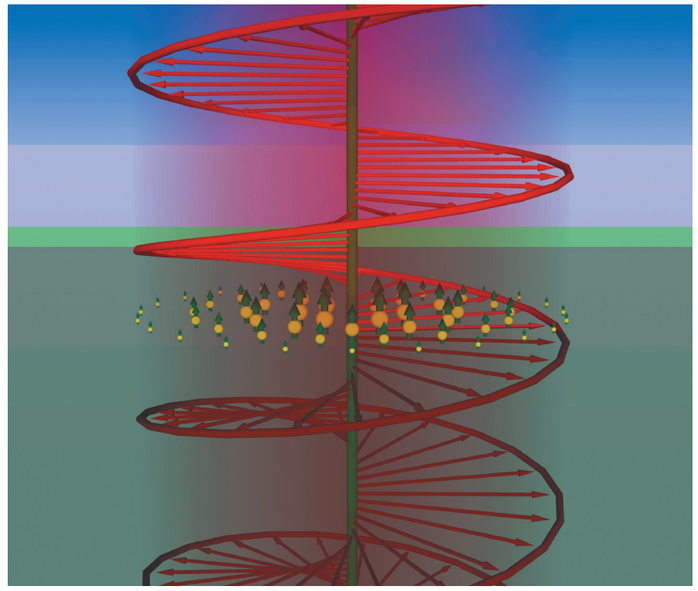
Researchers are working on developing a new breed of devices that will combine the advantages of light and electricity. Such devices will realize rapid, low-energy information processing by using photonic integrated circuits, where light is used to perform many of the functions currently realized electronically.

"Photonic integrated circuits are being developed for future fast and energy-efficient information processing by using light, because light is low loss and extremely fast," says Satoshi Iihama of AIMR at Tohoku University. "Many researchers are trying to implement optics in electronic devices."

Ideally, data would be stored in such devices by using light to switch the direction of magnetization in nanoscale magnets, but this has yet to be realized due to the weak interaction between light and magnetic materials.

Here, the researchers use helical laser beams to manipulate the magnetization in metallic ferromagnets—a technique based on the optical Rashba-Edelstein effect that has never been used on the interface between a ferromagnetic film and a non-magnetic heavy metal film (see Figure).

This way, the team has found a new method for generating spins optically at the interface of the two materials. The optical Rashba-Edelstein effect has not been demonstrated experimentally so far.



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A helical laser beam (red spiral structure) can induce spin (green arrows) at the interface of a magnetic (gray layer) and non-magnetic material (green layer).

"We tried to observe the optical Rashba-Edelstein effect experimentally using the interface between a ferromagnet and a heavy metal, and we discovered that there exists a coupling between optical helicity and electron spins even at a nanoscale interface," says Iihama. "This is the first time this has been demonstrated, and it came as a surprise to us."

"This study could lead to energy-efficient photonic–magnetic memory devices, and it could also open up a new research field that combines nanophotonics and spintronics," says Iihama. "As a next step toward realizing photonic-magnetic memory devices, we are planning to try to further increase the nanoscale photonic–spintronic coupling."

1. Iihama, S., Ishibashi, K. & Mizukami, S. Interface-induced field-like optical spin torque in a ferromagnet/heavy metal heterostructure. *Nanophotonics* **10,** 1169–1176 (2021).

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Co-researcher:
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MATERIALS CHEMISTRY

Published online on 26 April 2021

Chemical dealloying synthesizes new porous-carbon anode

A process that can fabricate a bimodal porous carbon and tune each modal pore size independently

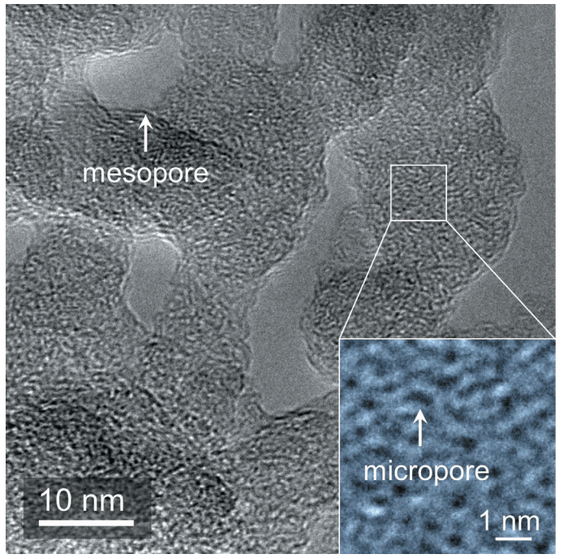
Researchers at AIMR have developed a sequential chemical dealloying technique for synthesizing 3D bimodal porous amorphous carbon with well-defined meso- and micropores[1]. With pore sizes and architecture tunable at the atomic scale, the amorphous-carbon product of this new, scalable process shows excellent performance as a sodium-ion battery anode.

The search for the next sodium-ion-battery hard-carbon anode is a quintessential transport problem. While numerous studies have shown that graphitic features such as surfaces, interlayers, and micropores can ameliorate sodium diffusion and storage, the sheer variety of hard-carbon defects makes the mechanisms difficult to elucidate.

That is, unless the improvement strategy targets a higher-performing hard carbon, whose 3D porous features are directly tunable by the novel fabrication method from the start.

"The main obstacle to exploiting dealloying for porous carbon synthesis is the strong chemical bonds and the high chemical stability of most carbide precursors," says Jiuhui Han, the first author of the study. "We overcame this obstacle by using a special Ni_3C precursor that is in a metastable phase at room temperature."

Using a two-stage dealloying process, the AIMR team produced a bimodal porous amorphous carbon. The first stage removes Mn from a $Ni_{30}Mn_{70}$ alloy, replacing it with carbon through carburization. The second stage removes Ni from the resulting metastable Ni_3C alloy, yielding an amorphous carbon with coexisting meso- and micropores.



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Transmission electron microscopy image of bimodal porous carbon showing the bicontinuous micropores (inset) in the ligaments of primary mesopores (main frame).

One key advantage of this method is that individual steps of the process control specific pore sizes, both at the meso- and at the micro-scale.

The team tested the performance of the new bimodal porous carbon as a sodium-ion battery anode. They found that not only does the product have rapid diffusivities, excellent rate capacities, and long cycling stability compared with known hard carbons, but its transport properties are affected by specific features that are process-controlled.

Future plans will utilize different metal-carbide precursors to expand the tailoring capabilities of this process. "Our DFT calculations of bond strength predict a broad range of metal carbides as potential precursors for preparing porous carbon by dealloying," says Han. "We will explore these metal carbides in the future."

1. Han, J., Li, H., Lu, Z., Huang, G., Johnson, I., Watanabe, K. & Chen, M. 3D bimodal porous amorphous carbon with self-similar porosity by low-temperature sequential chemical dealloying. *Chemistry of Materials* **33**, 1013–1021 (2021).

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Co-researcher:
Mingwei Chen

MAGNETIC MATERIALS

Published online on 31 May 2021

Hydrodynamics explore a soft material's magnetic handle

Tracing the nanoscale origins using mesoscale observations of a magnetic liquid

An AMIR-led team has used hydrodynamics experiments to investigate the magnetization of ferromagnetic liquid droplets[1]. The results show that the droplet remanent magnetization stems from the magneto-static short-range order (MSRO) between jammed magnetic nanoparticles, opening a new way to tailor the extraordinary material.

Ferromagnetic liquid droplets possess both solid-state magnetic properties and fluid-like shape-morphing capabilities thanks to the jamming of paramagnetic nanoparticle surfactants at liquid-liquid interfaces. This mechanism locks in the nanoparticles' MSRO, generating a remanent magnetization that makes biocompatible liquid robots a real possibility[2].

However, biocompatible capabilities such as targeted drug delivery or functional microfluidic channels entail the controlled shape changes and interactions with the environment at exquisite scales. Currently, too little is known about the MSRO origin of the droplet magnetization for such control.

"Magnetic short-range orders are difficult to measure directly," says Xuefei Wu from Beijing University of Chemical Technology. "They require magnetic imaging or scattering experiments that only provide local information."

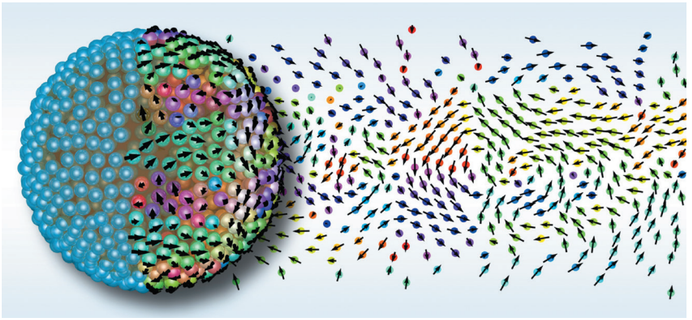
Instead, the team's approach to studying MSRO is to design hydrodynamics experiments that can directly measure the angular accelerations and velocities induced to spherical droplets by external magnetic fields.

"Our experiments are designed to inform us on how much magnetic torque the droplets experience," says Robert Streubel of the University of Nebraska-Lincoln. "Choosing spherical paramagnetic nanoparticles also enables the desired reversible transformation between paramagnetic and ferromagnetic liquids."

With this approach, the team has provided some intriguing evidence for MSRO, such as the pH of the droplets' aqueous phase controlling the amount of torque applied to the droplets, or the jammed nanoparticles enhancing magnetization by coupling with dispersed nanoparticles via magneto-static interactions—the same coupling that enables the additional assembly of non-magnetic nanoparticles while retaining substantial magnetization.

"The surprising thing about the remanent magnetization is that it emerges with the formation of the ferromagnetic liquid droplets," says Thomas Russell from AIMR. "This is the reason why droplet magnetization only requires low concentrations of magnetic nanoparticles and is preserved through droplet deformation."

Future directions will combine numerical modeling with hydrodynamics experiments to determine how the nanopatterning of the interfacial layer can tailor the droplet magnetization and functionalization.



© 2021 Thomas Russell

A spherical ferromagnetic liquid droplet showing the jammed iron oxide magnetic nanoparticles (blue circles on the left hemisphere). The arrows are the simulated macro spins illustrating the short-range magnetic order both in the right hemisphere of the droplet and on the background 2D projection.

1. Wu, X., Streubel, R., Liu, X., Kim, P.Y., Chai, Y., Hu, Q., Wang, D., Fischer, P. & Russell, T. Ferromagnetic liquid droplets with adjustable magnetic properties. *Proceedings of the National Academy of Sciences of the United States of America* **117**, e2017355118 (2021).
2. Fan, X., Dong, X., Lu, Z., Karacakol, A. C., Xie, H. & Sitti, M. Reconfigurable multifunctional ferrofluid droplet robots. *Proceedings of the National Academy of Sciences of the United States of America* **118**, 27916–27926 (2020).

Corresponding Researcher
Thomas P. Russell
Principal Investigator

GRAIN-BOUNDARY STRUCTURE

Published online on 28 June 2021

When microscopy and theory stretch beyond two dimensions

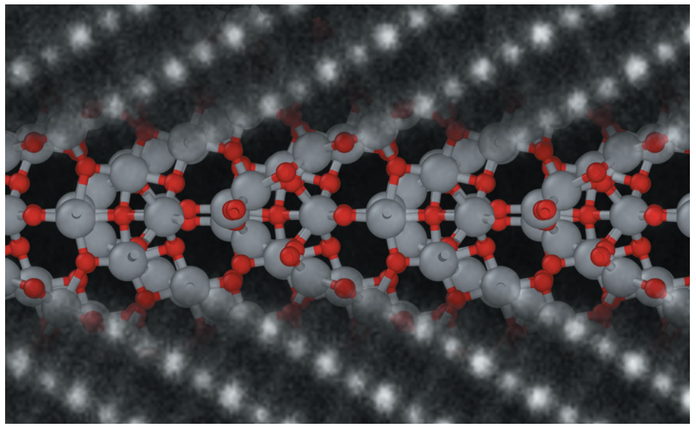
A synergistic approach that can elucidate complex interfacial structures

A collaboration between AIMR, the University of Tokyo, the University of York, and the University of Cambridge has demonstrated a new approach to investigating grain-boundary structures[1]. Combining scanning transmission electron microscopy (STEM) with ab initio random structure searching (AIRSS), the team has isolated a grain boundary with strong anatase character embedded in bulk rutile TiO_2, taking one more step toward bridging the structure-property gap in ceramics research.

Grain boundaries are ideal platforms for tailoring ceramic materials such as TiO_2. Ubiquitous in all but single-crystal solids, these interfacial structures are believed to be the sites of many processes such as dopant segregation, charge recombination, and domain migration—all potential solutions to engineering desired macroscopic properties of bulk materials.

However, while the traditional approach involving high-resolution imaging followed by computational optimization can elucidate simple grain-boundary structures, it cannot address more complex interfacial structures—where interesting physics happens—due to the 2D image limitations.

Here, the team led by Yuichi Ikuhara and Chris Pickard from AIMR, and Keith McKenna from the University of York takes a synergistic approach to broaden the scope of the grain-boundary structure investigation. Starting with imaging the grain boundary of a rutile TiO_2 bicrystal with high-resolution STEM, the team then uses AIRSS to explore the chemical environment adjacent to the imaged 2D structure.



Theoretical calculations help explore the interfacial structure between the two grains of a TiO_2 bicrystal (STEM HAADF image at top and bottom). The gray and red spheres at the center represent titanium and oxygen, respectively.

"Our initial local energy minimization methods failed to find a structure consistent with experimental STEM and electron energy-loss spectroscopy (EELS) observations," says McKenna. "Hence, we applied AIRSS, a global optimization method, to uncover the structure of the more complex TiO_2 grain-boundary structure."

This way, the team has predicted the local chemical environment of the imaged grain-boundary structure, calculated its EELS signals, and confirmed these signals experimentally. The results demonstrate that the grain boundary of the imaged bicrystal strongly resembles bulk anatase TiO_2—an impossible feat using the traditional modeling approach.

"Our study shows that the structures of complex interface systems are now within reach," says Georg Schusteritsch from the University of Cambridge. "We will use our method not only to elucidate these structures, but also to calculate their electronic, thermal, and mechanical properties for future interface designs."

1. Schusteritsch, G., Ishikawa, R., Razak Elmaslmane, A., Inoue, K., McKenna, K.P., Ikuhara, Y. & Pickard, C.J. Anataselike grain boundary structure in rutile titanium dioxide. *Nano Letters* **21,** 2745-2751 (2021).

Corresponding Researchers

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Principal Investigator

Chris J. Pickard
Principal Investigator

Co-researcher: Kazutoshi Inoue

CALCIUM BATTERIES

Published online on 26 July 2021

A step toward a high-energy density battery using an abundant, non-toxic alkali-earth metal

A designer electrolyte from concept to testing

A collaboration between AIMR, the Institute for Materials Research at Tohoku University, and the Laboratory of Materials for Renewable Energy at École Polytechnique Fédérale de Lausanne has designed, synthesized, and tested a new fluorine-free calcium monocarborane ($Ca[CB_{11}H_{12}]_2$) electrolyte[1]. With improved conductivity and electrochemical stability, the new electrolyte is a significant step towards realizing rechargeable calcium batteries.

Calcium batteries are prime candidates for replacing their lithium-ion counterparts because of calcium's abundance, non-toxicity, lower reduction potential compared to Mg or Al, and higher (Ca^{2+}) ionic charge capacity compared to that of Li^+.

However, the lack of a suitable electrolyte hinders the realization of calcium batteries with the above advantages.

Currently, cutting-edge model calcium batteries use fluorine-containing, weakly-coordinating electrolytes (e.g., $Ca(BF_4)_2$ or $Ca(B[hfip]_4)_2$ (hfip = hexafluoroisopropyloxy) in organic solvents) to maximize Ca^{2+} conductivity at the expense of electrochemical stability. Moreover, the presence of fluorine also results in the formation of a passivating CaF_2 film that prevents the reversible calcium plating/stripping at the anode surface.

To address these challenges, the team led by Kazuaki Kisu (currently affiliated to the Institute for Materials Research) and Shin-ichi Orimo from AIMR has designed a new electrolyte using monocarborane counterions (icosahedrons in Figure). Like the $Ca(BF_4)_2$ example, the new counterion is a weakly coordinating anion that maximizes Ca^{2+} conductivity; but unlike $Ca(BF_4)_2$, it is free from CaF_2 film forming.

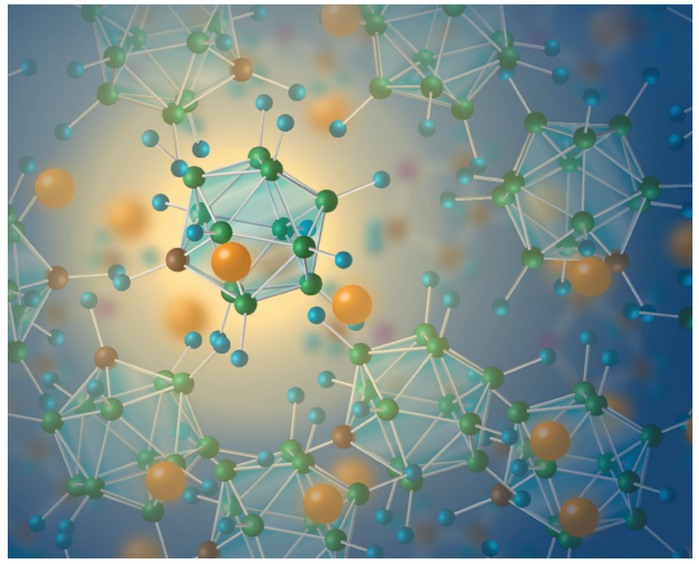

Illustration of the calcium monocarborane electrolyte. The yellow, green, brown, and blue spheres represent calcium, carbon, boron, and hydrogen atoms, respectively. The icosahedrons highlight individual monocarborane units.

"The monocarborane cluster is a stable, weakly coordinating counterion, but it is not soluble in many solvents," says Kisu. "We overcame this problem by using a mixture of desired solvents at specific ratios."

In this way, the team has synthesized the new electrolyte using a known scalable route. Preliminary tests of the electrolyte performances show promising results including high conductivity, wide electrochemical window, and reversible calcium plating/stripping without CaF_2 film formation.

"The test results from the new monocarborane electrolyte open a new path for other multivalent rechargeable-battery systems," says Orimo. "We are currently exploring the inclusions of other metals such as magnesium and aluminum."

1. Kisu, K., Kim, S., Shinohara, T., Zhao, K., Züttel, A. & Orimo, S. Monocarborane cluster as a stable fluorine-free calcium battery electrolyte. *Scientific Reports* **11,** 7563 (2021).

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Co-researcher:
Shin-ichi Orimo

GRAPHENE MESOSPONGE

Published online on 30 August 2021

Redesigning a fabrication method around a better template

How to make a proof-of-concept experiment scalable

An AIMR-led team has developed a scalable template-assisted method for fabricating edge-free, single-layer graphene mesosponge (GMS)[1]. Combining experiments with theory, the team has redesigned a known method using magnesium oxide (MgO) as template material instead of alumina (Al_2O_3). The use of MgO enables scalability and produces GMS with superior transport and mechanical properties compared with Al_2O_3.

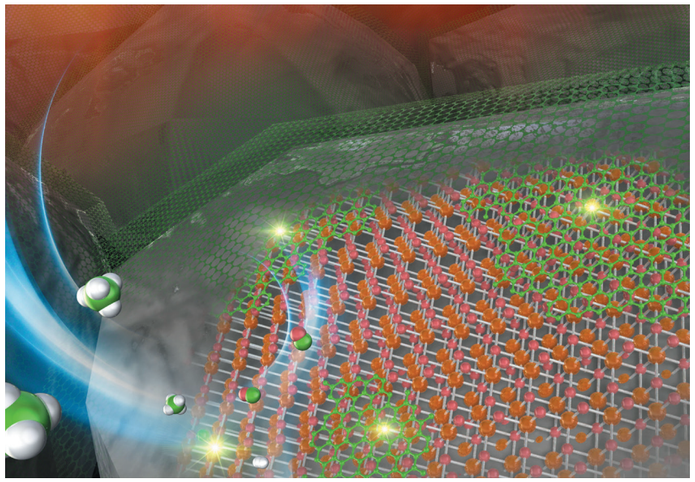
Proof-of-concept experiments often need major redesign before they are scalable.

One such example is the recent template-assisted fabrication of an edge-free, single-layer GMS that can outperform carbon nanotubes as supercapacitor electrode materials[2]. While this method produces a robust GMS, the removal of its Al_2O_3 nanoparticle template requires the drastic use of hydrofluoric acid that prohibits its commercial application.

Here, scalability entails redesign of the fabrication method around a different template—one that can both form the desired GMS and be removed in a cost-effective way. The team selects MgO nanoparticles.

"MgO is a commonly used template material in commercial porous-carbon productions; it is easily dissolved by dilute acid solutions," says Hirotomo Nishihara, the principal investigator from AIMR. "The trick is to make sure it can form GMS with the right features."

To this end, the team has used a combined experimental/theoretical approach to elucidate the GMS-formation mechanism and to establish the optimal conditions conducive to desired features such as single-layer graphene walls.



Adapted from Ref. 1 with permission from the Royal Society of Chemistry.

Representation of the graphene mesosponge synthesis via catalytic methane decomposition on magnesium oxide.

In so doing, the team has determined not only that the graphene-sheet formation likely occurs at oxygen vacancy sites on stepped MgO(110) facets, but also that the formation of the first graphene layer is much faster than that of subsequently stacked layers. This latter finding enables fine control of the reaction time for obtaining single-layer GMS.

Direct property comparisons indicate that the GMS produced using MgO is not only a good supercapacitor electrode material, but it is also more mechanically flexible than the GMS produced using Al_2O_3.

"We are investigating the use of other metal oxides and their effects as template materials beyond MgO and Al_2O_3," says Nishihara. "Ultimately, we are aiming for the development and the mass production of precisely controlled graphene nanomaterials."

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MATHEMATICAL MODELING

Published online on 27 September 2021

Making a link between graphene geometry and properties

A mathematical approach that connects experimental and theoretical observations

A research team led by AIMR has developed a mathematical model called standard realization with repulsive interaction (SRRI) that uses the geometric information of graphene to simulate its defect-induced curvatures and properties[1]. Experimental comparisons with the simulated properties suggest the possible use of SRRI as complementary pre-screening tool for both density functional theory (DFT) and experimental measurements.

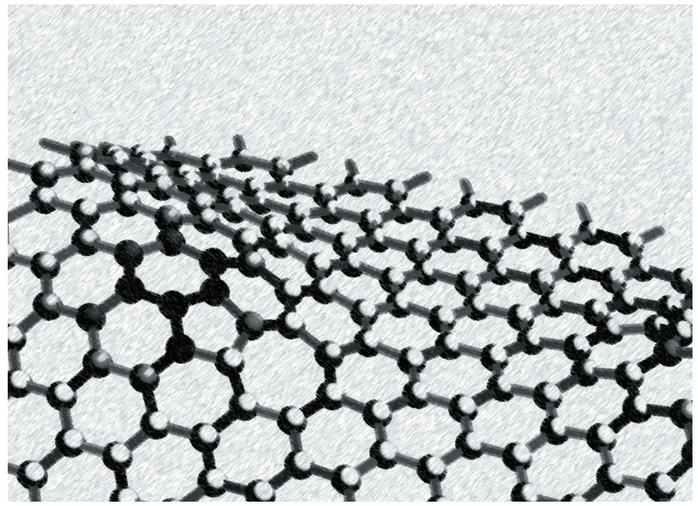
Scientists are still trying to understand how geometric changes in the graphene honeycomb structure can produce exotic properties.

For example, the introduction of topological defects by chemical treatments of graphene is known to both alter graphene geometry and enhance graphene catalytic properties. However, how these two observations are related to each other remains unclear.

Here, the team develops SRRI—a mathematical model that takes into account the attractive and repulsive interactions between graphene defects and their carbon-atom neighbors—to both simplify the model of interest and predict the curvatures and catalytic properties induced by graphene topological defects.

"Our approach refines an existing mathematical model[2] to describe the geometric changes in systems such as graphene and investigate their properties," says Yoshikazu Ito from the University of Tsukuba. "The resulting SRRI gives insight into the link between the geometry of the material and its properties."

Direct comparisons indicate that while SRRI predicts graphene defect-induced properties in qualitative agreement with DFT, it does so a billion times faster.



Representation of a graphene section with curvature induced by topological defects.

To demonstrate the significance of these results, the team synthesizes graphene samples with similar defects and uses scanning electrochemical cell microscopy to find a link between curvature and catalytic properties similar to those predicted by SRRI.

"Our results show a fast mathematical modeling method that not only can pre-screen model systems for in-depth DFT studies, but also could be used to guide experimental measurements in real time," says Motoko Kotani from AIMR.

Future projects will use SRRI to investigate the structure-property links of other carbon networks such as the Mackay crystal.

1. Dechant, A., Ohto, T., Ito, Y., Makarova, M. V., Kawabe, Y., Agari, T., Kumai, H., Takahashi, Y., Naito, H. & Kotani, M. Geometric model of 3D curved graphene with chemical dopants. *Carbon* **182**, 223-232 (2021).
2. Kotani, M. & Sunada, T. Standard realizations of crystal lattices via harmonic maps. *Transactions of the American Mathematical Society* **353**, 1-20 (2001).

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Principal Investigator

BAYESIAN STATISTICS

Published online on 25 October 2021

Deconvolving the many-body problem with numbers

First-time demonstration of a Bayesian approach to surface spectroscopic data analysis

A team led by AIMR has developed a new technique for interpreting surface electronic-states characterizations by modeling angle-resolved photoemission spectroscopy (ARPES) data using a Bayesian approach[1]. The team demonstrates this technique by confirming the size and by elucidating the microscopic origins of the $TlBi(S,Se)_2$ Dirac gap.

In condensed-matter physics, the many-body problem often complicates experimental measurements.

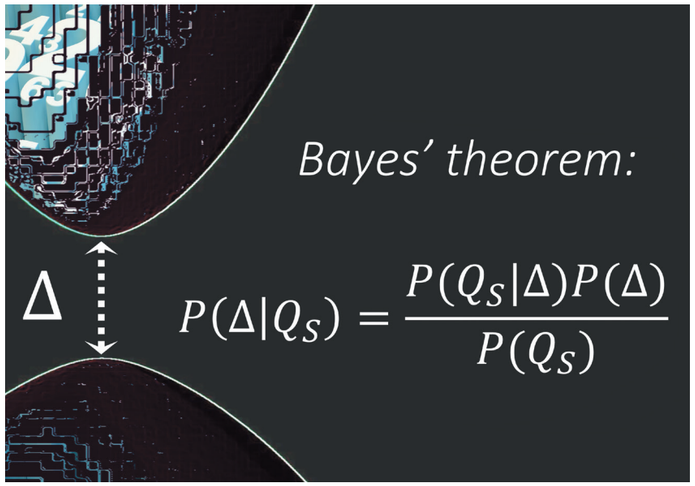
For example, the surface electronic states mapped by techniques such as ARPES are a convolution of the bare-band dispersions (E, single-electron dispersions) with the electron self-energies (Σ, multiple-electron correlations). This convolution makes graphene band gaps and dispersion kinks of high-temperature superconductors difficult to explain by ARPES measurements alone.

That is, unless each of the two components can be statistically extracted using known quantities.

Here, the team demonstrates an approach to investigating surface states by applying Bayesian modeling to the ARPES data acquired on a $TlBi(S,Se)_2$ surface—a material whose Dirac cone characterizations have been controversial due to the many-body problem.

"The Bayesian approach is very good at inferring the probability of any event, provided that quantities relevant to the event are either known, or can be modeled from real data," says Takafumi Sato, the principal investigator.

To this end, the team formulates a semiparametric Bayesian analysis expressing all relevant spectral quantities (Q_s, which include E and Σ) to model an ARPES map of $TlBi(S,Se)_2$. The modeling provides estimates for all Q_s, enabling the team to ask physical questions such as whether the $TlBi(S,Se)_2$ Dirac cones are gapped.



Using the Bayesian approach to investigate the Dirac gap size Δ. The posterior of the equation, $P(\Delta|Q_s)$, interrogates the probabilities of the Dirac gap having a size Δ for a given set of Q_s. The corresponding quantities $P(Q_s|\Delta)$, $P(\Delta)$, and $P(Q_s)$ used to calculate $P(\Delta|Q_s)$ are estimated from ARPES data.

Using Bayes' theorem (see Figure), the team calculated that the probability $P(\Delta|Q_s)$ of $TlBi(S,Se)_2$ having a gap of size $\Delta = 0$ is negligible, concluding that the bare-band $TlBi(S,Se)_2$ Dirac cones must be gapped.

"With this technique, we were not only able to calculate the Dirac gap size with high precision, but we were also able to narrow down the microscopic origins of the gap," says Sato. "This would not have been possible without the ability to deconvolve the many-body problem."

Future directions will apply this technique to other quantum materials to demonstrate its applicability.

1. Tokuda, S., Souma, S., Segawa, K., Takahashi, T., Ando, Y., Nakanishi, T. & Sato, T. Unveiling quasiparticle dynamics of topological insulators through Bayesian modelling. *Communications Physics* **4,** 170 (2021).

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HETEROGENEOUS CATALYSIS

Published online on 29 November 2021

Redirecting surface atom migration to the (100) facets of a ceria nanocatalyst

A new dissolution/re-precipitation method for recycling facet-controlled nanocatalyst

An AIMR-led research team has combined the use of an organic modifier with supercritical hydrothermal treatment techniques to design a strategy for regenerating facetted nanocatalysts[1]. The team demonstrates this strategy by regenerating degraded cubic ceria (CeO_2) nanoparticles back to their original cubic shape.

All heterogeneous catalysts degrade over time: poisoned by chemicals, fouled by carbon deposits, sintered by heat and pressure, or eroded by wear and tear. For this reason, the design of new catalysts often includes catalyst regeneration, aiming for regeneration methods that are clean, easy, and cheap.

However, while conventional regeneration approaches can ameliorate the above degradation mechanisms, they cannot address a mechanism particular to nanocatalysts—degradation through changes in surface facets.

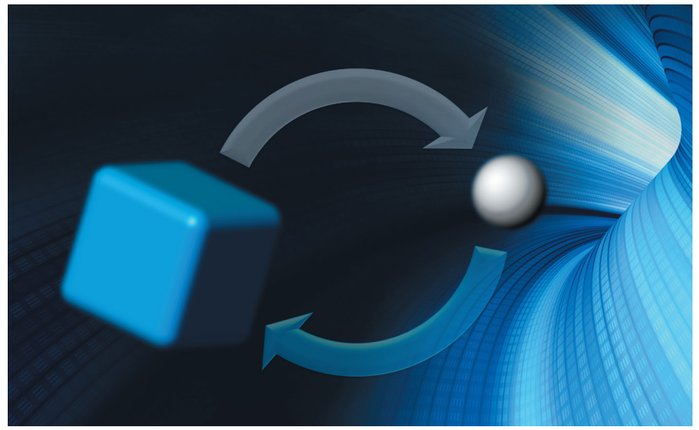
Here, the AIMR research team designs a regeneration approach aimed at reorienting active surface facets through partial dissolution-reprecipitation with a facet-selective organic modifier under supercritical hydrothermal conditions.

"CeO_2 nanoparticles are unique in that their shapes, exposed facets, and size distributions are controlled using carboxylic acids," says Takaaki Tomai, first author of the research. "To regenerate the (100) facet of the nanocatalyst, we use the decanoic acid surface modifier to control the exposed facet, and the formation of a Ce organometallic complex to promote dissolution in supercritical water."

Monitoring the particle size, shape, and catalytic activity by transmission-electron microscopy (TEM) and by oxygen storage capacity measurements, the team uses non-cubic CeO_2 nanoparticles to determine the optimum conditions for cubic-nanoparticle regeneration. The team then demonstrate the approach by degrading pristine cubic CeO_2 nanoparticles in air and restoring the cubic shapes to these same particles.

"Because our design involves complex particle-to-modifier interactions through partial dissolution and re-precipitation, none of us were sure whether it was going to work," says Tomai. "We were very excited to see the cubic shapes on the first TEM images of the regenerated nanoparticles."

Future directions will develop this simple nanocatalyst recycling approach to target several of the United Nations' 17 Sustainable Development Goals[2], including clean water and sanitation, affordable and clean energy, responsible consumption and production, and conservation of life below water.



A strategy for regenerating facet-controlled nanocatalysts. A cube-shaped nanoparticle model catalyst deteriorates (white arrow), losing its shape and catalytically active surfaces. The regeneration from the round-shaped particle (blue arrow) is achieved through partial dissolution-reprecipitation with a facet-selective organic modifier under supercritical hydrothermal conditions.

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2. https://sdgs.un.org/goals

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MOTTRONICS

Published online on 27 December 2021

Isolation of a robust room-temperature two-dimensional Mott insulator

Using low dimensionality to enhance Mott-transition temperature

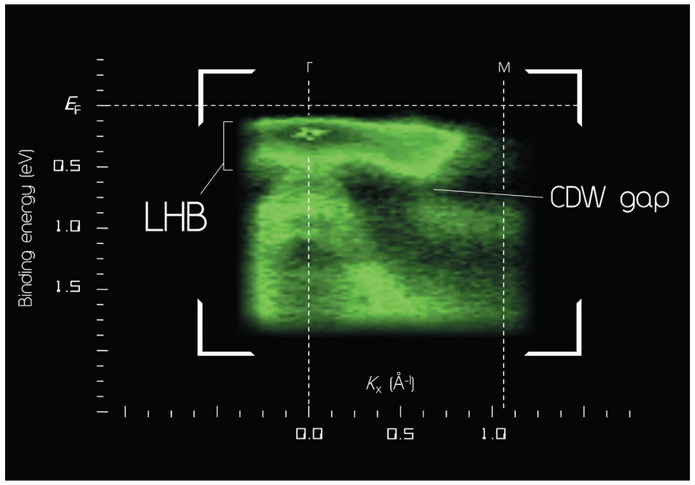
An AIMR-led team has isolated a room-temperature (RT), two-dimensional (2D) Mott-insulator phase of a single-layer 1T-$TaSe_2$[1]. Using angle-resolved photoemission spectroscopy (ARPES), the team has determined that the enhancement of the Mott-transition temperature stems from the interplay between exotic quantum features and low dimensionality. These results open a pathway toward the realization of RT Mottronic devices and high-temperature superconductors.

Superconductivity occurs in complex systems such as doped copper oxides (at T < 200 K) and tilted graphene bilayers (at T ~1 K). According to the Hubbard model, these superconductivity examples are associated with the Mott insulator—a phase that emerges when the electron correlation (U) of a material significantly exceeds the width of its partially filled band (W).

The Hubbard model also implies that the Mott transition of a material is triggered when physical conditions (e.g., temperature, pressure, and dopants) maximize the material's effective Coulomb interaction (U/W), suggesting a strategy toward RT Mott-transition: maximizing U/W using low dimensionality.

Here, the team demonstrates this strategy using 2D transition-metal dichalcogenides (TMDs) such as the single-layer 1T-$TaSe_2$.

"Because the bulk 3D 1T-$TaSe_2$ undergoes Mott transition at low T (< 200 K), reducing its dimensions to 2D should raise its U/W value, enhancing the Mott-transition temperature," says Takafumi Sato, the principal investigator. "The key lies in designing a set of experiments that can demonstrate this possibility."



Valence-band ARPES intensity along the ΓM cut for the monolayer 1T-$TaSe_2$. The labels "LHB" and "CDW" stand for lower Hubbard band and charge density wave, respectively.

To this end, the team combines ARPES with other spectroscopic techniques to monitor U/W-defining electronic features. While the simultaneous observation of the Mott gap and the charge-density-wave (CDW) gap at T = 40 K suggests that the 2D 1T-$TaSe_2$ is a Mott insulator, the observation of the lower Hubbard band up to T = 450 K indicates the Mott-insulator phase is robust at RT and beyond.

"We have discovered a unique, 2D RT Mott insulator phase," says Sato. "This is only possible thanks to an exquisite interplay where U is enhanced by exotic features such as CDW, and W is reduced by 2D confinement."

Future work on 2D TMDs will aim at demonstrating the Mott-insulator to metallic phase transitions at RT, and at detecting high-temperature superconductivity.

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