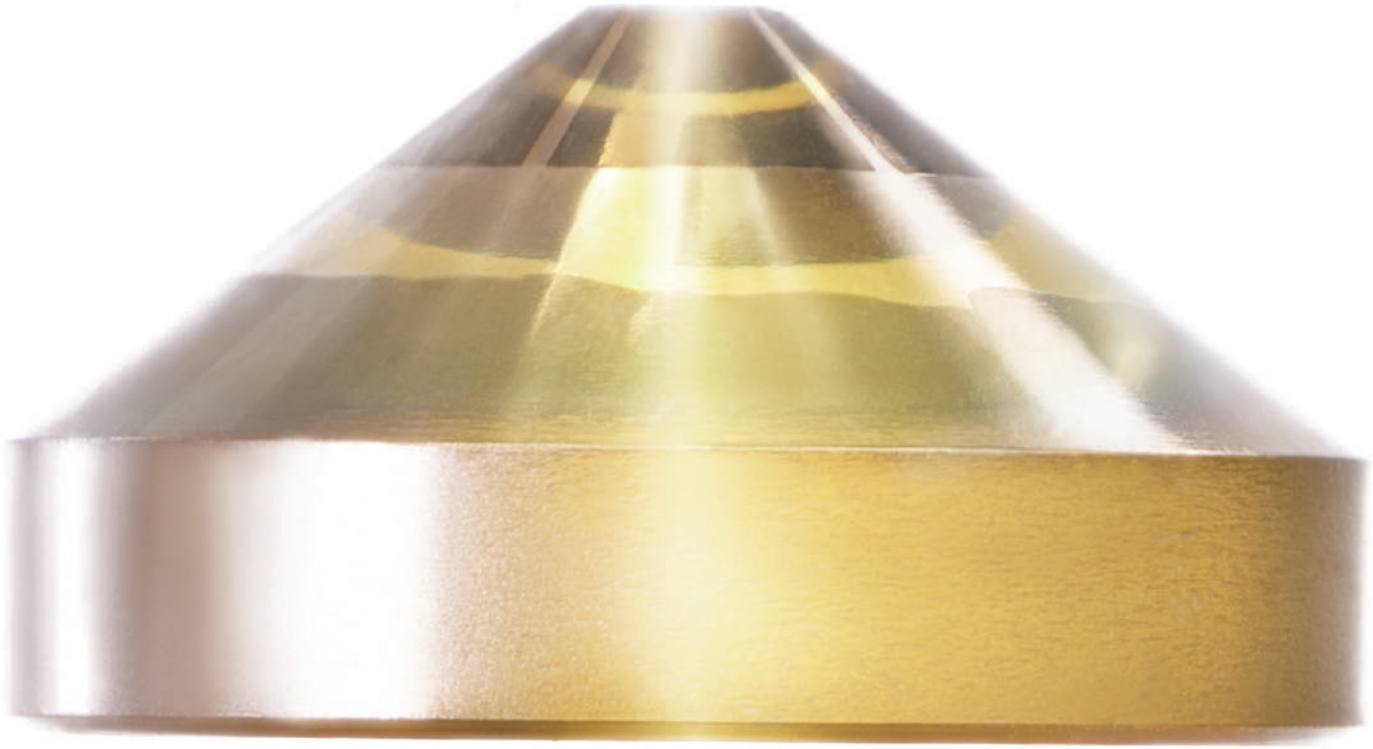
NATIONAL INSTITUTE FOR MATERIALS SCIENCE

NIMS NOW INTERNATIONAL

2024 No.2

Research Center
for Materials
Nanoarchitectonics
(MANA)

Exploring new frontiers with Nanoarchitectonics



Exploring new frontiers with Nanoarchitectonics

Create, arrange, and combine nanostructures of atoms and molecules.
And architecting materials with innovative functions that cannot be achieved with a single material.
We call this process "nanoarchitectonics."

Quantum mechanical phenomena are becoming increasingly prominent as materials are miniaturized.
Research Center for Materials Nanoarchitectonics (MANA)
will not only sow the seeds for technologies
that go beyond conventional concepts through the exploration of "nanomaterials,"
but will also establish the fundamentals of quantum technology through the creation of "quantum materials."

MANA will realize its vision of the future, and go beyond what people can imagine.
MANA will expand the world from nano.

Data : **Research Center for Materials Nanoarchitectonics (MANA)**

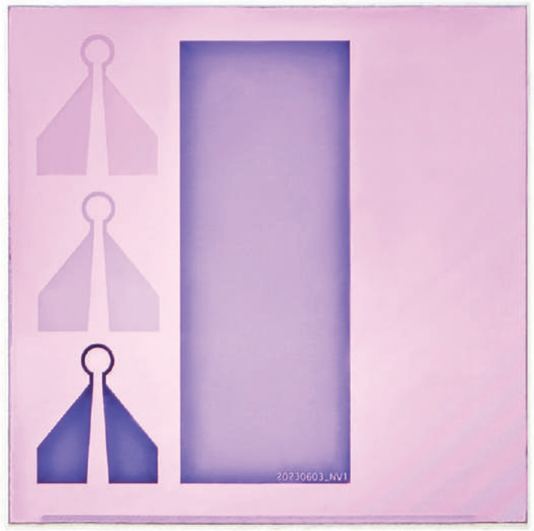
Director : Takashi Taniguchi 
Number of permanent researchers: 84

Quantum Materials Field

- Frontier Superconducting Materials Group
- Quantum Solid State Materials Group
- Quantum Device Engineering Group
- 2D Quantum Materials Group
- Surface Quantum Phase Materials Group
- Quantum Material Properties Group
- Quantum Materials Modeling Group
- Quantum Materials Simulation Group
- Topological Quantum Materials Theory Group
- Nanostructured Semiconducting Materials Group
- Photonics Nano Engineering Group
- Thin Film Electronics Group
- Qubit Materials Group
- Ionic Devices Group

Nanomaterials Field

- Soft Chemistry Group
- Functional Nanomaterials Group
- Layered Nanochemistry Group
- Frontier Molecules Group
- Thermal Energy Materials Group
- Functional Chromophores Group
- Supermolecules Group
- Nanoparticle Group
- High-Pressure Structural Controls Group
- ElectroActive Materials Team
- Optical Nanostructure Team



Cover Story

Diamond anvils for high-temperature, high-pressure experiments.

Diamond indenters (anvils) are positioned facing each other to sandwich the sample, and loads are applied from both sides. This generates an ultrahigh pressure, approaching the pressure in the depths of the Earth. Since lasers and X-rays can penetrate the anvils, heating, crystal structure analysis, and characterization become feasible under ultrahigh pressure. What is notable about the anvil in the cover photo is that electrodes for electrical resistance measurement are patterned near the tip of the lower anvil (as shown in the photo ① on this page, viewed from above). Ryo Matsumoto has developed technology to form a circuit of diamond with a high concentration of boron added to the tip of a diamond anvil, which is utilized in the search for materials, including superconducting materials. Incidentally, this yellowish diamond is "Hime-DIA," the world's hardest material, provided by Professor Tetsuo Irifune of Ehime University, a joint researcher. It withstands the application of higher pressure than ordinary diamonds (see p. 10).

① ② ③ ④ (actual size) A diamond anvil with circuits formed is seen from above. ① "Hime-DIA " with patterning of electrodes for measuring electrical resistance (described on the left page). ② Brilliant-cut diamond (single crystal as well as ③ and ④) with patterning of heater and thermometer for heating in addition to electrodes (schematic diagram on p. 10). The tip plane is only 0.3 mm in diameter and can apply approximately 100 GPa. ③ The purple diamond contains NV centers, which are expected to be applied to quantum sensors. ④ The planar-shaped diamonds represent the initial type that successfully measured electrical resistance for the first time utilizing the formed electrodes. Subsequently, circuits were successfully formed into conical shapes resembling ① and ②.

Key Projects

Read on for an overview of the research projects being carried out at the Research Center for Materials Nanoarchitectonics (MANA).

#1 Basic and fundamental research for creating new functions through quantum architectonics.

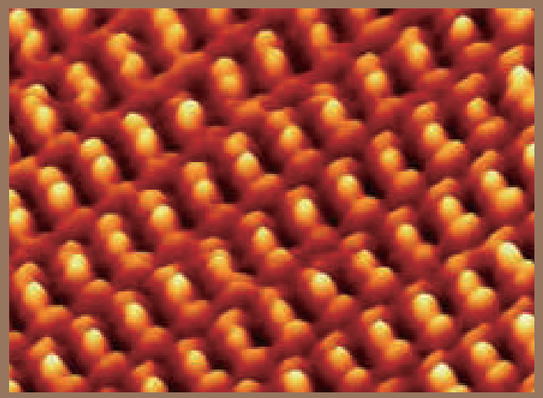
Project leader
Naoki Fukata

Creating a driving force for quantum innovation

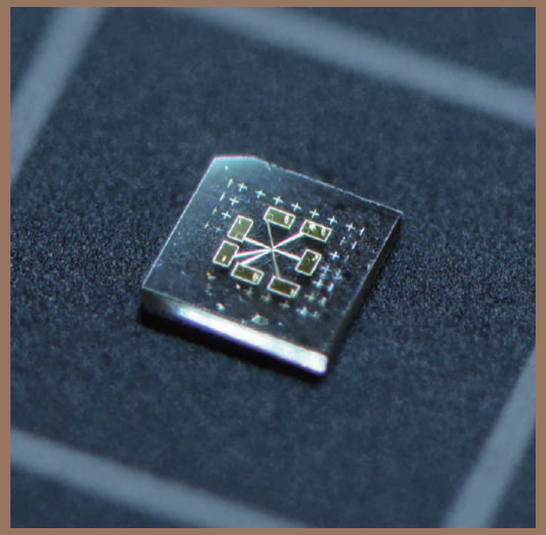
Material Creation and Condensed Matter Theory

When materials are reduced to the nanoscale, peculiar phenomena governed by the laws of quantum mechanics emerge. The creation of "quantum materials" that actively utilize such quantum phenomena is one of NIMS' priority themes, and MANA plays a central role in NIMS. MANA tackles the challenge of discovering unknown quantum phenomena and creating new materials by precisely controlling interfaces using nanotechnology for superconductors, strongly correlated materials, low-dimensional materials, and more. Additionally, MANA aims to create novel functions by forming heterojunction and novel alloy structures with different nanomaterials and to advance evaluation technologies, such as for exploring quantum phenomena at cryogenic temperatures. Furthermore, by combining theoretical and numerical simulations, the behavior of electrons, photons, and spins, which are the sources of quantum states, will be thoroughly clarified and elucidated their relationship with the structure of materials.

See Research 1 on **p. 6**
See Research 2 on **p. 9**
See Research 3 on **p. 10**



STM image of an indium atomic layer grown on the surface of a silicon substrate.



"Diamond transistor" utilizing h-BN thin film as a gate insulator to achieve high mobility.

Laying the Foundations for Quantum Device Applications

Realization of quantum functions

Within the project for the creation of quantum materials, research and development focused on quantum device applications are also underway. Examples include "quantum dots," responsible for information processing in quantum computers and photon oscillation in quantum cryptography, and thin-film transistors, offering superior performance to conventional electronic devices. Additionally, we are addressing emerging challenges towards realizing innovative quantum devices, such as devices for brain-type information processing utilizing ion transport phenomena in matter. We are also advancing nanofabrication technology to realize these devices. We will not only lay the foundation for Japan's national policy, the "Quantum Technology Innovation Strategy," but also create new values that break through existing concepts.

#2 Developing new functional materials through nanoarchitectonics.

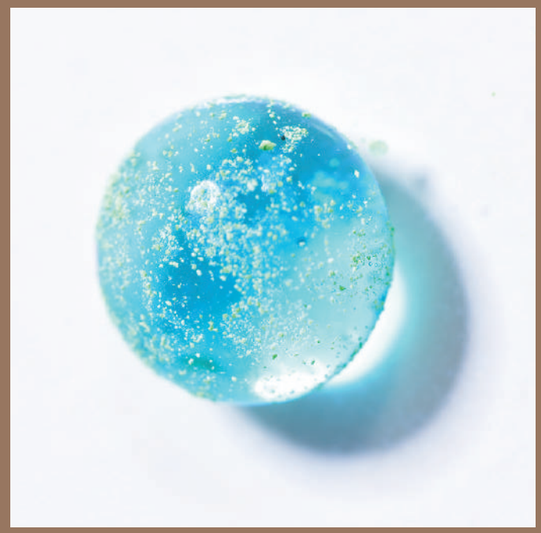
Project leader
Takao Mori

Material creation through design and control of nanostructures

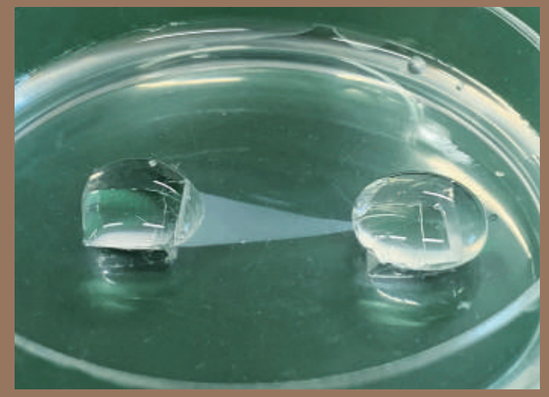
Structural Design

While the Quantum Materials project (see #1 on the left page) focuses on fundamental research in quantum technology, this project will apply "nanoarchitectonics" to a broader array of functional nanomaterials. Even the smallest differences in size, shape, or stacking of nanostructures can lead to dynamic changes in physical properties. To facilitate flexible material design and unlock novel functions, we will advance nanostructure fabrication and control technologies. Our targets and approaches encompass diverse techniques, including structuring and integrating nanomeshes, supramolecules, and iron oligomers through chemical synthesis, as well as controlling material structures via ultrahigh pressure applications, for example. MANA is committed to creating unique materials by precisely controlling nanospaces and interfaces.

See Research 6 on **p. 15**



Liquid marble, droplets coated and encapsulated with a hydrophobic powder.



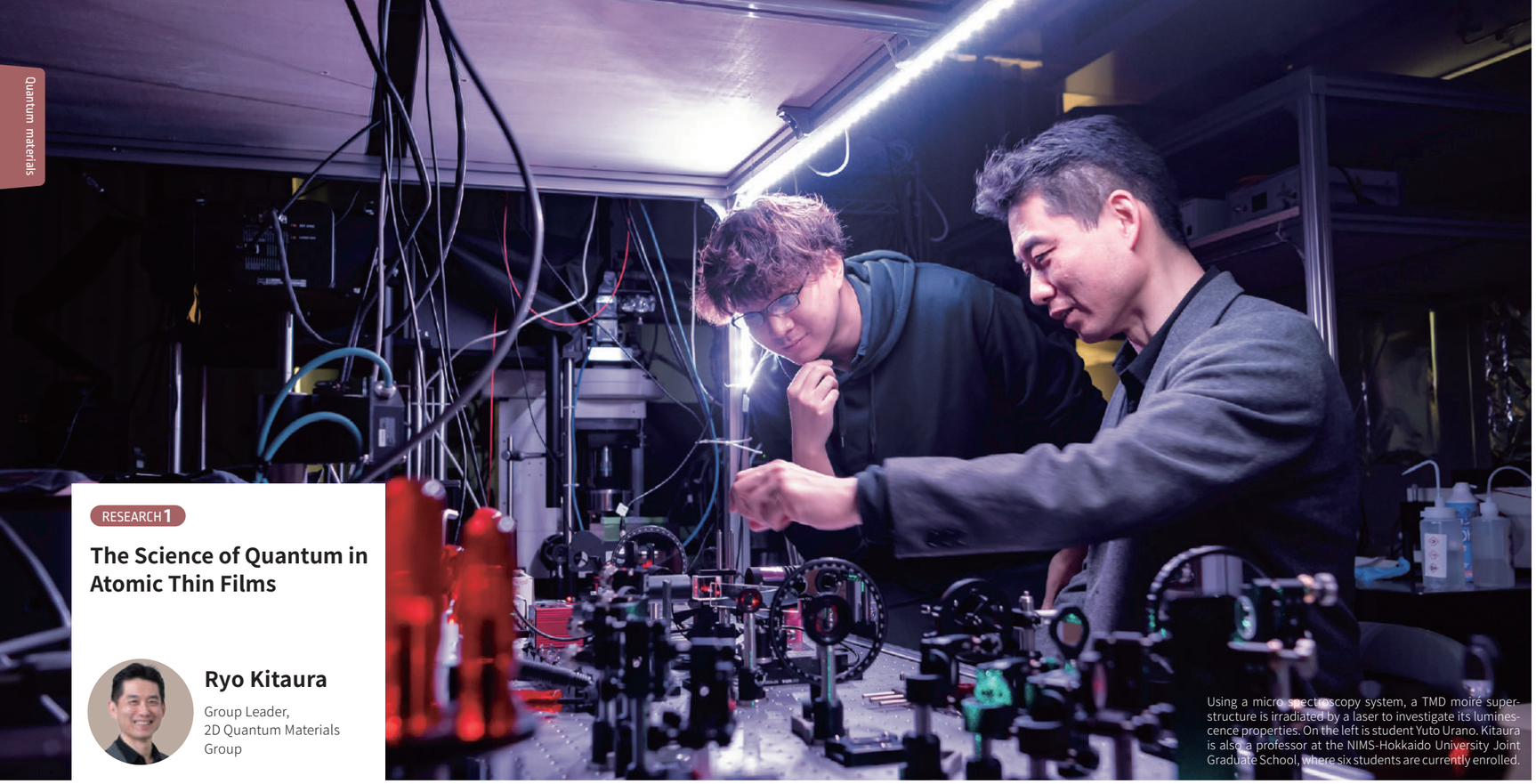
Ion transport device using nanosheets with the world's highest anion conductivity (at the center is a triangle-shaped nanosheet membrane).

Enhancing material functions and creating innovative functions

Functional design

The functions of nanomaterials are governed by phenomena such as electronic states, propagation and interactions of photons and phonons. By manipulating these phenomena, MANA aims to achieve higher performance and significantly enhance the functionalities of various materials, including thermoelectric materials, sensors, catalytic materials, and photoelectric materials. To this end, we promote strategic research and development by incorporating theory, simulation, and data science, as well as developing state-of-the-art evaluation equipment and conducting in-situ analysis. Additionally, we will actively pursue the exploration of novel functionalities. Furthermore, we will explore a new fusion area together with the structural design field (see left), by actively incorporating different types of materials into functional design strategies, and by striving for synergistic effects of heterogeneous materials and functions. This approach will lead us to create groundbreaking materials and devices, contributing to the advancement of various technological fields and the resolution of social issues.

See Research 4 on **p. 11**
See Research 5 on **p. 14**



Using a micro spectroscopy system, a TMD moiré superstructure is irradiated by a laser to investigate its luminescence properties. On the left is student Yuto Urano. Kitaura is also a professor at the NIMS-Hokkaido University Joint Graduate School, where six students are currently enrolled.

RESEARCH 1

The Science of Quantum in Atomic Thin Films

Ryo Kitaura

Group Leader,
2D Quantum Materials Group

Low-dimensional materials, which have a thickness of only one to several atoms, exhibit several strange quantum mechanical properties that are not found in ordinary materials. Ryo Kitaura advocates for research aimed at designing their structure and understanding their physical properties, as well as developing devices driven by novel principles.

Amazing discoveries published in 2018

Graphene, discovered in 2004, is a sheet-like material made of carbon atoms arranged in a honeycomb pattern. It is only one carbon atom thick. Graphene is being studied for various purposes because of its high strength and flexibility, as well as its excellent electrical and thermal conductivity. Two-dimensional materials, such as graphene, which are less than one nanometer or only a few atoms thick, are currently piquing the curiosity of many scientists.

One of them, Kitaura, who continues to explore the science of low-dimensional materials based on two-dimensional materials, recalls, "In 2018, a research group from the Massachusetts Institute of Technology and Harvard University presented sensational research results at the American Physical Society (APS). I happened to be in the audience listening to the presentation, and it was astonishing. I have been totally fascinated by this field of research ever since."

The talk was about how two layers of graphene stacked at different angles to form a structure called a "moiré superlattice (figure 1)" can produce completely different electrical properties from a singlelayer graphene. Moiré is an interference pattern that appears when two atomic layer-thin films are stacked at different angles. By slightly changing the twist angle, entirely different electrical properties, such as superconductivity, can be obtained.

"This phenomenon is not unique to graphene. If you stack two layered materials with periodically arranged atoms and twist them slightly, you get moiré, and quantum mechanical properties that are not found in ordinary materials will emerge. The research topic on which we have been focusing is the creation of new technologies, namely quantum technologies, that leverage these properties." says Kitaura.

What is an "artificial atom" created by overlapping two-dimensional materials?

Currently, the "2D Quantum Materials Group" led by Kitaura is focusing on the moiré superlattice structure of a two-dimensional material called "transition metal dichalcogenide (TMD). This material has a structure

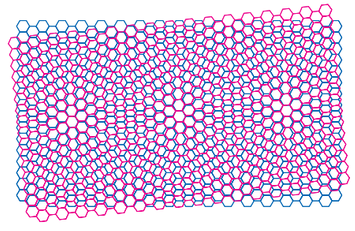


Figure 1. Schematic diagram of a moiré superlattice
An interference pattern that appears when two low-dimensional materials with periodic structures are stacked.

in which a layer of transition metal atoms is sandwiched between layers of chalcogen atoms. Unlike graphene, TMDs exhibit semiconducting properties even in a single layer and have been actively studied in recent years as a material that could lead to the creation of ultra-compact devices.

"If you look at the moiré pattern of a two-dimensional material from a distance, you can see a large pattern (long period structure). Interestingly, each large pattern behaves as if it were a single atom. This phenomenon is called an 'artificial atom,' and serves as the basis for various physical properties. For example, by confining an electron-hole pair into an artificial atom (quantum confinement), it can be used as a quantum light source that transmits photons and serves as an information carrier in quantum cryptographic communication," explains Kitaura.

Speaking of quantum light sources, the memory of "quantum dots" is still fresh in our minds, as the Nobel Prize in Chemistry was awarded to three American scientists in 2023. Quantum dots are nanometer-sized semiconductor particles. As the size of the semiconductor particle decreases, the range in which electron waves can exist is limited. As a result, the color of the light emitted and absorbed by the particles changes as a function of particle size due to quantum mechanical effects (see related research on p. 11). Similarly, we can control the waves of electrons trapped in artificial atoms within a moiré superlattice and use them as a new quantum light source.

Advanced thin-film fabrication technology to realize nanostructures as desired

However, it requires extremely advanced technology to arrange atoms and create nanostructures as envisioned. Since the interaction of each atom is used and to create a functionality, high-quality crystals without defects are essential. Kitaura has been working on improving thin film deposition techniques called "molecular beam epitaxy" and "metal-organic chemical vapor deposition (MOCVD)." These methods are mainly used in the fabrication of compound semiconductors such as TMDs.

The MOCVD system (see photo) is particularly suitable for TMD deposition, as it is capable of depositing films by supplying organometallic materials and gases as raw materials. Kitaura has made various improvements to this equipment, such as increasing the number of elements that can be handled and improving controllability by monitoring during deposition. As a result, Kitaura has succeeded in fabricating high-quality TMD with precisely controlled thickness at the atomic level.

"We are currently tackling the challenge of forming and characterizing new moiré superlattices by growing TMD monolayer

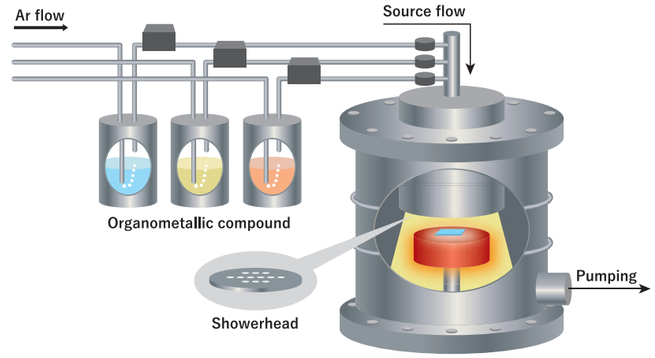
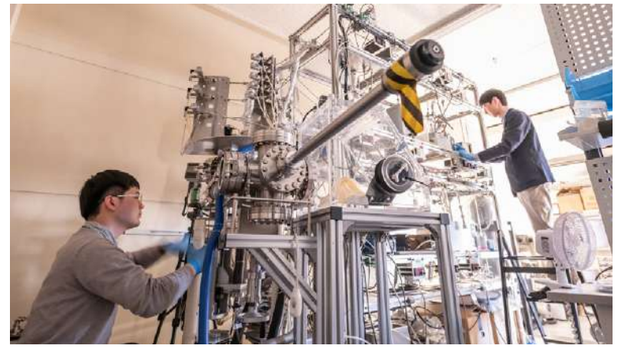


Figure 2. Schematic diagram of a MOCVD system
Liquid organometallic compounds containing raw material metals (such as tungsten (W) and molybdenum (Mo)) are gasified by feeding argon gas, which is supplied to the reactor with increased vapor pressure. The gas is provided from a shower head directly above the substrate. Decomposition and chemical reaction proceeds on the substrate, promoting crystal growth.



Feng Zhang (left) and Junpei Okuda (right) , students of the NIMS-Hokkaido University Joint Graduate School, operate the MOCVD equipment. The reactor is on the left in the photo.

composed of different compounds bonded in-plane and further stacking them (figure 3). In previous research, we have succeeded in bonding single-layer molybdenum disulfide (MoS_2) and tungsten disulfide (WS_2) using our independently developed MOCVD system to obtain atomically flat interfaces. Furthermore, we have succeeded in stacking these structures. By utilizing first-principles calculations and a microspectroscopy measurement system (see the photo on p. 6), we have confirmed that quantum confinement effects occur in the artificial atoms of the stacked structure and that new optical responses emerge. In the future, we would like to improve the precision of bonding and stacking further to design an array of artificial atoms and utilize the quantum mechanical phenomena that occur there, leading to innovative quantum devices. We aim to tackle the ultra-fine wiring on the nanoscale by leveraging the state-of-the-art microfabrication equipment available at NIMS. I aspire to present new possibilities as many as possible of the potential afforded by technologies unique to us. To accomplish this, we will persist in advancing both basic and applied research on low-dimensional materials, which harbor boundless possibilities," Kitaura says emphatically.

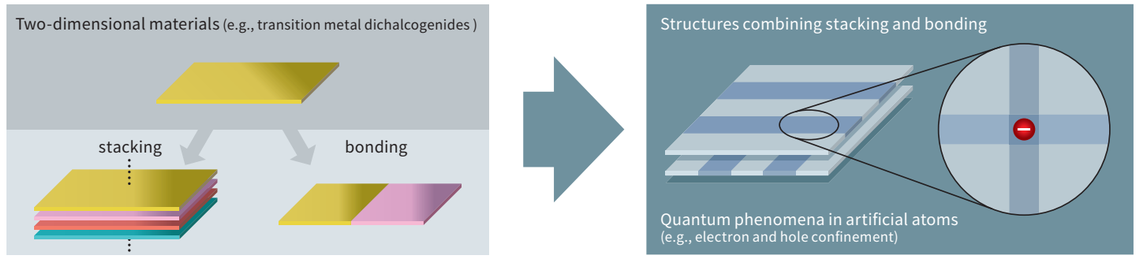


Figure 3. Design of materials and structures based on embedding low-dimensional states (artificial atoms)

About MANA

MANA is an international research center established at NIMS with the support of the World Premier International Research Center Initiative (WPI), a project initiated by the Ministry of Education, Culture, Sports, Science and Technology (MEXT) in 2007. After 10 years of support by the program, MANA became the "WPI Academy" to make great strides as the world's leading nanotechnology materials research center.

MANA Satellite Network

MANA introduced the "Satellite" system to implement the internationalization of our research environment. We invited prominent researchers as Satellite PIs, and established MANA satellites at each research institute to strongly support world-class research of MANA. These satellites also provide young researchers at MANA an international research training ground, with satellite PIs working as their mentors.

■Quantum Materials Field

Large-scale Order-N DFT Calculations

David Bowler

University College London

■Quantum Materials Field

Molecular Device Engineering

Christian Joachim

The French National Centre for Scientific Research

■Nanomaterials Field

Fuzzy Assembly

Gero Decher

Strasbourg University

■Nanomaterials Field

Transmission Electron Microscopy, Nanotubes

Dmitri Golberg

Queensland University of Technology

■Nanomaterials Field

Nanoscale Chemistry

Thomas E. Mallouk

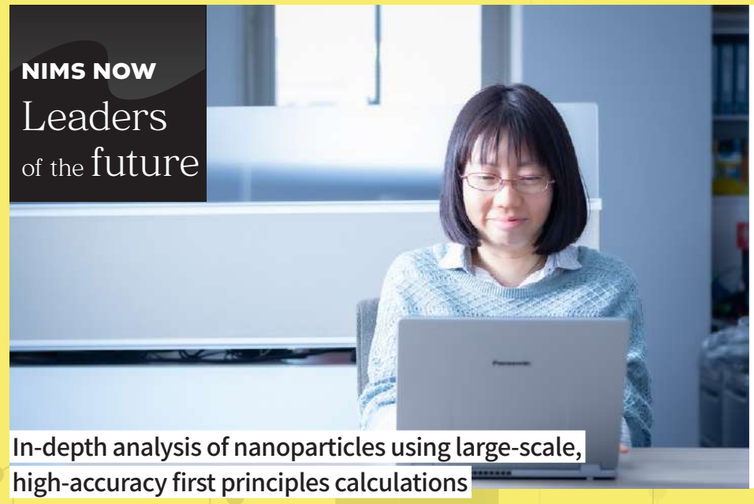
University of Pennsylvania

■Nanomaterials Field

Inorganic total synthetic chemistry, Conductive porous materials

Yusuke Yamauchi

The University of Queensland



In-depth analysis of nanoparticles using large-scale, high-accuracy first principles calculations

Ayako Nakata
Principal Researcher,
Quantum Materials
Simulation Group

First principles calculations can be used to accurately simulate the atomic-scale structures of materials and predict their electronic states. Ayako Nakata and her colleagues succeeded in developing a calculation technique applicable to a wider range of materials than conventional calculation techniques. This was achieved by reducing the number of necessary calculations, which previously increased cubically as the number of atoms to be considered increased. Nakata has since been using this technique to analyze nanomaterials.

Evolving CONQUEST: a large-scale first principles calculation computer program

Quantum mechanics-based first principles calculations can be used to unravel interactions taking place between atoms and electrons within materials. They are especially useful in accurately simulating the atomic-scale structures of materials and predicting their electronic states while they are being exposed to extremely high temperatures and/or pressures—conditions under which actual measurements are difficult to take. The biggest issue with first principles calculations, however, is that the number of calculations needed increases by an amount roughly equivalent to the third power of the number of atoms to be taken into account. For example, when the number of atoms to be included in the calculation increases by 10 times (e.g., from 10 to 100), the number of calculations increases by approximately 1,000 times, posing a great challenge to many computational scientists.

NIMS, the University of London in the UK and the University of Bordeaux in France jointly developed CONQUEST—a large-scale first principles calculation application—in an effort to enable first principles calculations to take a greater number of atoms into account while reducing the rate at which the number of necessary calculations increases. The order-N method CONQUEST employs is able to reduce the number of necessary calculations to be linear to the number of atoms (for example, when the number of atoms increases by 10 times, the number of calculations increases also by 10 times).

"CONQUEST was rolled out in 2020 and has been updated several times since," said Nakata, one of CONQUEST's developers. "In a recent update, we developed multisite support functions and incorporated them into CONQUEST. This addition enabled the program to perform calculations that take a significantly larger area of a material into account."

A noteworthy improvement enabled by this addition is that the upgraded CONQUEST is readily capable of carrying out large-scale (i.e., involving thousands of atoms), high-accuracy first principles calculations targeting metals and materials with no bandgap—tasks that were virtually impossible using conventional techniques. With this new capability, CONQUEST is now applicable to all classes of materials regardless of electrical conductivity (e.g., insulators, semiconductors and metals).

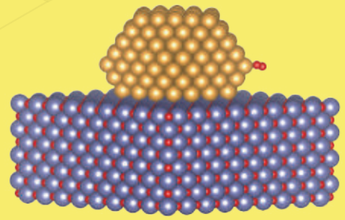
Meticulously analyzing metallic nanoparticle catalysts

Using CONQUEST, Nakata and her colleagues have been conducting numerical calculations focused on different types of materials, including metallic nanoparticle catalysts. These catalysts—composed of a metallic nanoparticle affixed to the surface of a metallic oxide carrier—can be used to accelerate various chemical reactions, including hydrogen producing reactions. Their catalytic activities are greatly affected by the sizes of the nanoparticles and the interactions between nanoparticles and their carriers.

"In addition to these factors, catalytic activities are significantly influenced by electron transfers involved in catalytic reactions," Nakata said. "Because first principles calculations are a powerful tool for analyzing electrons in materials, they can be useful in guiding the development of high-performance catalytic materials. The incorporation of multisite support functions into CONQUEST enabled it to perform calculations on a scale as large as an actual nanoparticle catalyst."

Nakano's recent research focused on a catalyst composed of a gold (Au) nanoparticle 2 nm in diameter affixed to the surface of a magnesium oxide (MgO) carrier. She used multisite support functions to analyze how the structure and electronic state of the catalyst may change as the size and shape of its Au nanoparticle change (figure). As a result, she found that the interaction between an Au nanoparticle and its carrier can cause changes in the atomic-scale structures of both. She also ascertained how the sizes and shapes of Au nanoparticles influence the electronic states of the catalysts.

"Although these findings are significant, there are still many unknowns concerning Au nanoparticle catalysts," Nakata said. "Results produced by large-scale first principles calculations are complex to interpret and identifying the factors that influence catalytic activities from them is not an easy task. I hope to find ways of efficiently identifying other key factors— possibly by using machine learning and/or other strategies."



Simulated image of a metallic nanoparticle catalyst

Large-scale first principles calculations were performed to simulate various Au nanoparticle catalyst shapes by affixing differently-shaped Au nanoparticles 1 or 2 nm in diameter to the surfaces of MgO carriers. These differently-shaped catalysts were then subjected to calculations to predict their structural stability and electronic states. This diagram shows a simulated catalyst with an Au nanoparticle 2 nm in diameter to which an O_2 molecule (red circles) has been attached through adsorption.

RESEARCH 3

NIMS NOW
Leaders of the future

Ryo Matsumoto

Ryo Matsumoto
Researcher,
Frontier Superconducting Materials Group

Diamond circuits enable efficient materials searches under extreme high-pressure, high-temperature conditions

A diamond anvil cell (DAC) can be used to recreate the extremely high pressures—reaching hundreds of thousands of atmospheres—that exist deep inside the Earth. This device makes it possible to synthesize and take physical property measurements from material samples under extreme high-pressure, high-temperature conditions. Ryo Matsumoto has developed a new DAC capable of easily adjusting the temperature of a material sample while it is being measured. This device has significantly streamlined Matsumoto's efforts to find high-performance superconducting materials.

Shortcomings of conventional DACs

"The crystalline structures of materials change under different pressure and temperature conditions," said Matsumoto, who has been developing new DACs suited to his efforts to identify superconductors with desirable characteristics—his main research focus. "These relationships can be exploited to synthesize materials with different crystalline structures. DACs enable efficient materials searches under extremely high-pressure, high-temperature conditions."

DACs are often used in experiments in which material samples need to be simultaneously subjected to extremely high pressures reaching hundreds of thousands of atmospheres and high temperatures. A material sample is first placed between two diamond anvils. These anvils then compress the sample. A DAC can also be used to synthesize a material sample under extremely high-pressure, high-temperature conditions by projecting a laser beam through the transparent diamond anvils and the sample between them, thereby heating the sample. In addition, DACs have been used to take measurements from material samples under extreme high pressures (e.g., analyzing a material sample's crystalline structures using x-rays and measuring its electrical resistance by attaching electrodes to it).

"However, it was difficult to precisely control the temperature of material samples with existing DACs," Matsumoto said. "Another issue arose when I needed to apply greater pressure to a material sample. This could be done by significantly reducing the size of a sample while also reducing the surface areas of the diamond anvil tips that come into contact with it. However, attaching electrodes to a miniaturized sample so that its physical properties can be measured is extremely difficult. To overcome these issues, I formed electrode, heater and thermometer circuits on the surface of a diamond anvil."

Developing a high-performance, durable diamond anvil

Matsumoto formed electronic circuits made of a diamond doped with high concentrations of boron (i.e., boron-doped diamond (BDD)). BDDs have some unique properties. For example, their electrical conductivity increases as their boron content increases. BDDs also become superconductive at very low temperatures. NIMS has extensive experience in studying the physical properties of BDDs and has developed BDD film deposition techniques.

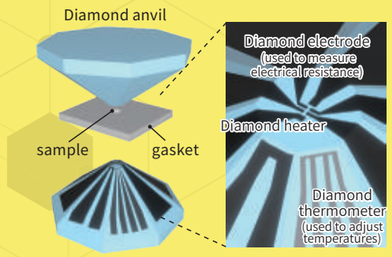
Matsumoto formed electronic circuits on the surface of a diamond anvil by leveraging film deposition techniques NIMS developed. He first imprinted circuit-patterned masks onto the anvil surface using electron beam lithography and deposited a BDD thin film on the masked surface using the chemical vapor deposition (CVD) process. These circuits enabled Matsumoto to take precise measurements from a material sample while precisely controlling its temperature (figure).

Matsumoto explained how challenging it was to form these circuits on the curved surface of a conical diamond anvil. He had to adjust the CVD parameters many times before finally figuring out the right values to uniformly deposit a BDD thin film over the surface of the diamond anvil from the tip to the sides. He also had to deal with another issue: because diamond has high thermal conductivity, heat applied to a diamond anvil quickly dissipates. Taking this property into account, Matsumoto carefully selected materials to use for the DAC parts surrounding the diamond anvil. After about four years of trial and error with a lot of supports from other researchers and students, Matsumoto finally completed fabricating a DAC capable of meeting his research needs.

He has since been using the DAC in his search for superconductors with the potential for practical use.

"Many new materials with superconducting properties have been predicted using first principles calculations," Matsumoto said. "Many have yet to be synthesized because they need to be synthesized under extremely high-pressure, high temperature conditions. Using the DAC I developed, I succeeded in synthesizing a difficult-to-manufacture superconductor made of tin sulfide (Sn_3S_4) and ascertained the relationship between its superconducting properties and its crystalline structures."

More than 100 years have passed since the superconductivity phenomenon was discovered. However, no superconductor products available for use by the public have yet been brought into existence. Matsumoto's ultimate ambition is to discover and commercialize a revolutionary superconductor. The DAC he developed may help him achieve this dream.



Schematic diagram illustrating the electronic circuits Matsumoto formed on the surface of the lower diamond anvil

An example of the electronic circuits made from boron-doped diamond Matsumoto formed on the surface of a diamond anvil. A heater circuit is used to heat a material sample being synthesized and a thermometer circuit is used to adjust its temperature. Because the anvils and circuits are both made from diamond, they are extremely durable and can withstand repeated use.

RESEARCH 4

Precision synthesis technology paves the way for a promising future in the realm of "nanoparticles"

Naoto Shirahata
Group Leader,
Nanoparticle Group

The fabrication of quantum dots by a method known as the "hot injection method", which is widely applied to the synthesis of colloidal nanoparticles. Organometallics, the raw material for quantum dots, are rapidly injected into a hot solvent. Particle size can be adjusted by heating time.

Quantum dots are ultrafine particles with diameters of only a few nanometers. They exhibit unique optical properties due to the behavior of electrons confined in a very small space. Naoto Shirahata and his colleagues have achieved significant advancements in the research and development of quantum dots themselves and "hybrid nanoparticles" with modified surfaces. They are now aiming to apply these materials in a wide range of fields, spanning from optoelectronics to biotechnology.

Quantum dots, zero-dimensional materials

When semiconductor crystals are made into much smaller, nano-sized particles, they start emitting light. Semiconductor ultrafiner particles showcasing such unique properties are termed "quantum dots." Due to their nano-sized nature as "dots," they are also referred to as zero-dimensional materials.

Generally, once a material is determined, the emission color is unambiguously determined. Quantum dots, on the other hand, emit and absorb light at different wavelengths simply by changing their size. This is due to a phenomenon known as the "quantum confinement effect." Moreover, they are already being used in displays and other applications due to their high color purity and excellent luminous efficiency.

However, quantum dots in existing products contain highly toxic elements such as cadmium (Cd) and lead (Pb). Shirahata et al. are therefore trying to create quantum dots with high luminous efficiency/absorption using RoHS compliant elements, and to extend the color gamut that can be handled by their dots. They are also working on the fabrication of device prototypes.

Toward the development of environmentally and biologically friendly materials

Around 1990, it was discovered that silicon (Si) crystals, when particulated to diameter 5 nm or less, emit a dark red light. The discovery of luminescent silicon raised high hopes for the realization of light sources in silicon photonics, a technology expected to enable faster processing than conventional electronic circuits. Additionally, since silicon is abundant on Earth and non-toxic to the environment and living organisms, it is anticipated to broaden the applications of quantum dots, such as in the field of biotechnology. However, at that time, their luminous efficiency was only a few percent, and they were far from practical use. Since then, "silicon quantum dots" have become a major focus in semiconductor research, and Shirahata et al. have been working on improving their luminous efficiency.

Shirahata's focus was to identify the "defects" that were reducing the luminous efficiency. Using a variety of analytical techniques, he discovered that the quantum dot surface is covered by an amorphous film with a non-periodic arrangement of atoms. Shirahata then surmised that the unbound atoms in the amorphous structure that had lost their covalent bonding partners would correspond to the defects responsible for reducing the luminescence efficiency. He, then, tried to stabilize the silicon quantum dots by binding other molecules or ions (ligands) to the defects.

"The solution was to modify the silicon surface with organic molecules. We discovered that these organic molecules act as anchors

for the silicon surface, thus preventing amorphization. By 2010, the luminous efficiency of silicon quantum dots had been increased up to 60%. We were able to expand the wavelength range of current-driven light-emitting diodes (LEDs) devices using these quantum dots as the active layer, extending it from the previously limited range of 700-800 nm to 590-1000 nm," Shirahata recalls.

These quantum dots, in which functions such as luminous efficiency are enhanced in a non-linear manner by precisely combining organic and inorganic materials, are referred to by Shirahata as "hybrid nanoparticles." Since then, the development of the quantum dots and the processing method for hybridizing them have been the focus of Shirahata and his colleagues' research.

Extended emission colors of silicon quantum dots

One of the achievements related to quantum dots themselves is the expansion of the luminescence color range dependent on the size of the silicon quantum dots, which was announced in 2020.

"In addition to the scientific impact of transforming indirect transition semiconductors such as silicon, which inherently lack luminescent properties, into strong emitters through nanosizing, research on silicon quantum dots has advanced worldwide amidst restrictions on hazardous substances. There was a long running debate about luminescence peak wavelength range which that can be controlled by size. In most of published papers, the emission colors that can be modulated by size control of diamond cubic silicon quantum dots are limited to orange, red, and near-infrared, corresponding to 590-1050 nm. However, I focused on the fact that the size dependence of luminescence has been little discussed for silicon quantum dots smaller than 2 nm." Shirahata said.

Silicon quantum dots emitting red light have a diameter of approximately 2 nm. However, Shirahata et al. undertook the challenge of synthesizing smaller quantum dots with diamond cubic structure and succeeded in developing new quantum dots that emit green, green-yellow, and yellow light, depending on their size. They achieved this by creating six different sizes ranging between 1.1 and 2 nm in diameter, expanding the library of quantum dots (see photo).

Silicon quantum dots can now replicate a broad spectrum of emission regions, spanning from near-infrared to visible to near-ultraviolet light. The focus is now shifting towards enhancing carrier mobility and devising methods for achieving long-term stable emission for practical applications.

"Coherent core-shell structures" leading to higher quality III-V semiconductor quantum dots

In 2022, high-quality quantum dots using indium phosphide (InP), one of III-V semiconductors, were also being developed.

Group III-V semiconductors are suitable for the active layer of photodetectors due to their high carrier mobility. However, when group III-V semiconductors are fabricated into quantum dots, defects are generated on the surface and a photocurrent cannot be extracted because the defects act as a trapping source (i.e., nonradiative recombination channels) for carriers. Consequently, InP quantum dots have not been utilized in devices.

To solve this problem, Shirahata et al. presented a new nanostructure called "coherent core-shell." This is a structure in which the core crystal is covered by a shell crystal just like an egg (figure). Although the core and shell are dissimilar semiconductors, their crystal lattices expand and shrink relative to each other to form a quasi-single-crystal structure so that they have the same lattice constant.

Shirahata et al. employed hybrid nanoparticles with indium phosphide quantum dots in the core and zinc sulfide in the shell as the active layer of a photodiode, successfully extracting them as photocurrent to an external electrode. This success stems from the fact that the photo-excited carriers generated in the core crystal can propagate throughout the core-shell structure.

"Indium phosphide has a larger lattice constant than zinc sulfide by as much as 7%. Therefore, simply covering it with zinc sulfide would result in numerous defects at the interface. In this situation, computer simulations confirmed that 'if the thickness of the zinc sulfide is reduced to about 3 atoms, lattice constant matching occurs at the interface and a defect-free structure can be created.' We solved the lattice mismatch problem by developing a synthesis process to realize the zinc sulfide neatly covering InP with a thickness of about three atoms." Shirahata said.

The development of this technology has expanded the range of available semiconductors, including other III-V systems.

Focus on nano-bio applications

Shirahata highlights his strengths, stating, "They lie in the precision synthesis technology of nanocrystals." In the future, he will also explore the application of "his original" quantum dots.

"When you shine light on a quantum dot, the surface modification method of the core quantum dot differs depending on whether you want to convert it into electricity, generate heat, or convert electricity to heat... depending on the desired function. Now that we have accumulated knowledge of all synthetic methods, we aim to develop materials that can contribute to society." Shirahata said.

The applications being explored include optoelectronic devices such as LEDs and photodetectors, as well as photothermal conversion devices that convert light into heat, and even cancer theranostic devices. For instance, the company is currently focusing on optimizing hybrid nanoparticles with applications such as cancer vaccines combined with drug delivery systems in mind.

Shirahata remarks, "We aim to maximize the resourcefulness and environmental and human health benefits of these materials and apply them to nano-bio applications."

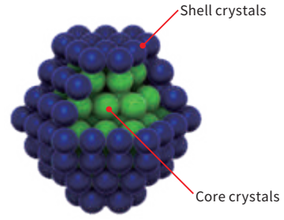
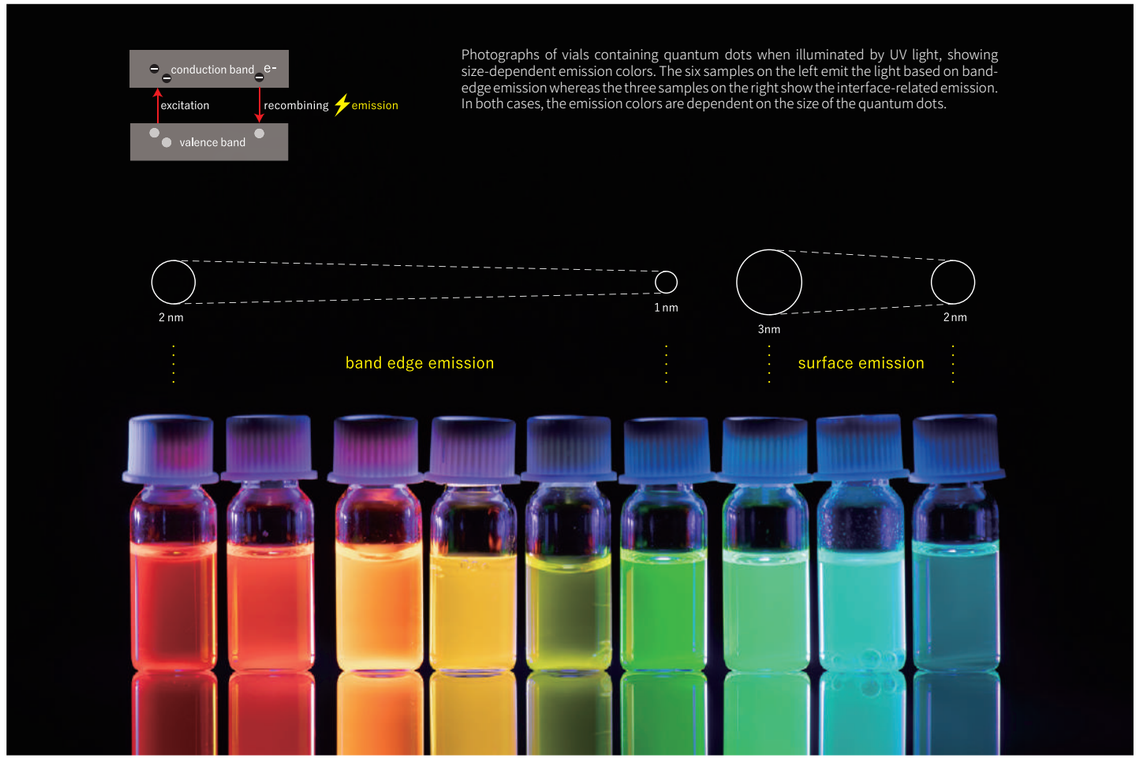
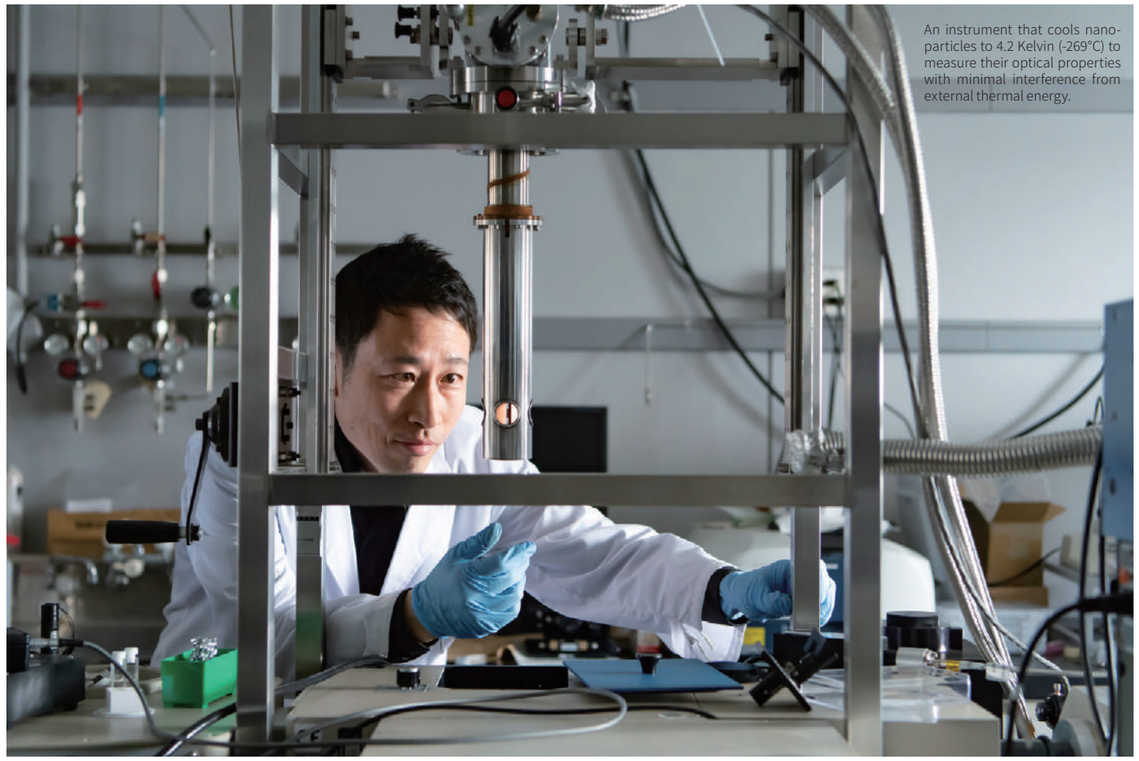


Figure
Schematic diagram of coherent core-shell structure.



Photographs of vials containing quantum dots when illuminated by UV light, showing size-dependent emission colors. The six samples on the left emit the light based on band-edge emission whereas the three samples on the right show the interface-related emission. In both cases, the emission colors are dependent on the size of the quantum dots.



An instrument that cools nanoparticles to 4.2 Kelvin (-269°C) to measure their optical properties with minimal interference from external thermal energy.

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Elucidation of a mechanism drastically suppressing heat transport in solids towards enhancement of thermoelectric conversion efficiency based on theoretical calculations

Naoki Sato

Researcher,
Thermal Energy
Materials Group

Massive amounts of waste heat are constantly released from various sources into the environment. NIMS has been researching and developing thermoelectric materials capable of directly converting waste heat into electricity. A material NIMS developed using only relatively abundant, less toxic elements achieved one of the highest thermoelectric efficiencies ever recorded. We asked Naoki Sato—who revealed a mechanism of thermal transport in the developed material—how it was achieved.

Sluggish advances in thermoelectric materials R&D

The Seebeck effect is a phenomenon that involves the direct conversion of a temperature difference between two dissimilar conductors or semiconductors into an electric voltage, and vice versa. This effect has been the subject of worldwide thermoelectric materials R&D since its discovery more than 200 years ago. Despite these extensive efforts, practical use of these materials is still uncommon.

Heat is significantly more difficult to control than electricity. Highly efficient conversion of temperature differences into electricity requires materials that simultaneously exhibit low thermal conductivity and high electrical conductivity. However, most materials with high electrical conductivity also exhibit high thermal conductivity.

Bismuth-tellurium (Bi-Te)-based and lead-tellurium (Pb-Te)-based materials currently exhibit state-of-the-art thermoelectric efficiencies. In particular, Bi-Te-based materials held the record for the highest near-room-temperature thermoelectric efficiency for more than half a century. However, these materials remain unpopular because they contain toxic and scarce Te.

More recently, a Japanese private company developed a magnesium-antimony (Mg-Sb)-based thermoelectric material composed entirely of more abundant, less toxic chemical elements. This achievement was published in 2016, attracting a great deal of interest from the global thermoelectric research community. However, the near-room-temperature thermoelectric efficiency of this material was far lower than that of Bi-Te-based materials, motivating many researchers to develop higher-performance Mg-Sb-based materials.

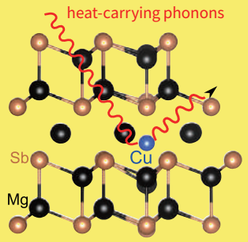
Interstitial atom avoiding heat transport discovered by simulations

Phonons are major heat carriers in solids. A phonon is a quantized expression of atomic vibrations within a crystalline lattice. Phonons carrying heat in solids have a wide distribution of characteristic length depending on materials, typically from atomic scale to the order of meters. Thus, phonon-mediated thermal conductivity is influenced by various interacting factors, including crystalline defects and materials' microstructures. Controlling the thermal conductivity of materials therefore requires comprehensive control of these factors, posing a great challenge. In 2021, "Thermal Energy Materials Group" in NIMS successfully developed a novel Mg-Sb-based material with addition of a tiny amount of copper (Cu) exhibiting superior thermoelectric performance compared with previously reported ones, which was comparable with the Bi-Te-based materials. The developed Mg-Sb-based material not only demonstrated improved electrical conductivity but also surprisingly reduced thermal conductivity. Sato managed to solve the mystery—how heat is disrupted in the material.

"I simulated atomic and electronic behaviors based on first principles calculations," Sato said. "A common approach to improve thermoelectric properties of previously reported Mg-Sb-based materials was to substitute some of the constituent elements with different elements. However, in case of our developed material, my simulation results suggested that a Cu atom is inserted into an interstice of a crystalline lattice, rather than a substitution for an occupied atomic site."

Sato further investigated these results by performing another round of first principles calculations. He identified the optimal position in the crystalline lattice for the insertion of Cu and simulated how this affected the heat-carrying phonon states. As a result, he revealed that the inserted Cu caused local distortions of the crystalline lattice, leading to the phonon states that effectively disturbed heat transport (figure).

"The insertion of Cu into the interstice of lattice, which is a slight change in atomic scale, can drastically reduce thermal conductivity," Sato said. "Moreover, further enhancement of thermoelectric performance requires precise structural control at different scales, from nano to micro-level. Computational simulations and theoretical calculations are powerful tools to optimize such complex situations of materials developments. My next ambition is to discover new thermoelectric materials with even higher performance by a combination of different tools." Sato aims to develop highly efficient, environmentally friendly, non-toxic thermoelectric materials—the ultimate goal of many scientists in this field—by leveraging leading-edge techniques.



Schematic of an atom inserted into interstice of crystalline lattice disrupting thermal transport

In the Mg-Sb-based material, Cu atom can be inserted into a specific site, which effectively disturbs heat-carrying phonons, leading to the significant reduction of thermal conductivity.

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Simple, precise aqueous solution-based doping technique for organic semiconductors

Yu Yamashita

Researcher,
Supermolecules Group

Organic semiconducting materials have been used to fabricate lightweight, flexible, potentially inexpensive printable semiconductor devices. However, their use in certain industrial sectors is limited due to a lack of simple, precise doping techniques for them. In October 2023, Yu Yamashita and his colleagues published a research article reporting a breakthrough organic semiconductor doping technique they developed.

Doping techniques vital to improving semiconductor performance

Most semiconductor devices on the market are made of silicon—an inorganic semiconducting substance. Semiconductors can be either p- or n-type. P-type semiconductors use holes as their majority charge carriers while n-type semiconductors use electrons. Either type of silicon semiconductor can be produced by adding small amounts of other chemical elements to it (i.e., doping) which are incorporated into the silicon crystal lattice. Doping is a crucial process in controlling the electrical conductivity of semiconductors for use in high-performance electronic devices.

Simple, precise doping techniques suitable for use in fabricating commercial- and consumer-grade organic semiconductors did not exist before the breakthrough by Yamashita's team. For the first time in the world, Yamashita and his colleagues succeeded in developing a precise, aqueous solution-based doping technique applicable to organic semiconductors. This achievement attracted a great deal of attention when it was first reported in a research paper in October 2023.

"Organic semiconductors have traditionally been doped chemically by allowing them to react with redox agents," Yamashita said. "However, conventional redox agents needed to be handled in an inactive gas atmosphere or a vacuum due to their high reactivity and susceptibility to moisture and other substances present in the air. Such chemical doping of organic semiconductors also lacks precision and stability. Furthermore, the crystalline structure of organic semiconductors is developed only by weak intermolecular interactions, where dopant molecules need to be incorporated without disrupting the crystallinity Developing new redox agents capable of overcoming these issues had been extremely challenging, seriously hampering efforts to put organic semiconductors into practical use for certain applications."

Gaining inspiration from photosynthesis and other biochemical reactions

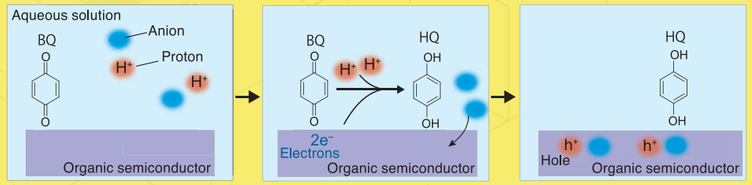
Yamashita found clues to resolving these issues in the biochemical reactions occurring in biological systems. Redox reactions within living organisms are always precise and stable regardless of changes in external ambient moisture.

Inspired by this fact, Yamashita focused on proton-coupled electron transfer (PCET)—a concerted reaction that involves the transfer of negatively charged electrons (e^-) and positively charged protons (H^+) from one molecule to another. PCET reactions are sensitive to the pH (i.e., the concentration of H^+) of the aqueous solution in which they take place. In other words, PCET reactions can be precisely controlled by adjusting the pH of the solution.

Yamashita experimentally doped organic semiconductor thin films by immersing them in an aqueous solution containing benzoquinone (BQ) and hydroquinone (HQ)—two chemical compounds suitable for PCET reactions—and $TFSI^-$ anions as a p-type dopant (figure).

This experiment demonstrated that the electrical conductivity of organic semiconductors can be precisely controlled by adjusting the pH of the aqueous solution. Yamashita also confirmed that the holes and $TFSI^-$ anions added to the organic semiconductors were stably incorporated into their crystalline structures without disrupting them.

"This doping technique is very easy to implement; you need only immerse organic semiconductor thin films in an aqueous solution to dope them," Yamashita said. "Key to our success was our completely unconventional approach; rather than using conventional redox agents in water-free environments to prevent them from reacting with water, we used hydrophilic redox agents in aqueous solutions." Yamashita's flexible thinking has opened up new horizons for the future of organic semiconductors.



Chemical doping process for organic semiconductors in an aqueous solution

This aqueous solution contains benzoquinone (BQ) and hydroquinone (HQ)—two organic compounds acting as redox agents—and $TFSI^-$ dopant anions. Polymeric organic semiconductor thin films are first immersed in this solution (left). This induces a proton-coupled electron transfer (PCET) reaction, in which BQ accepts two electrons from the organic semiconductor and two protons from the solution to transform into HQ (middle). As a result of this PCET reaction, holes are created in the organic semiconductor. The $TFSI^-$ anions are incorporated stably into the thin film through electrostatic interactions, completing the p-type doping (right).

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on the cover: Diamond anvils for high-temperature, high-pressure experiments (see p.3)

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