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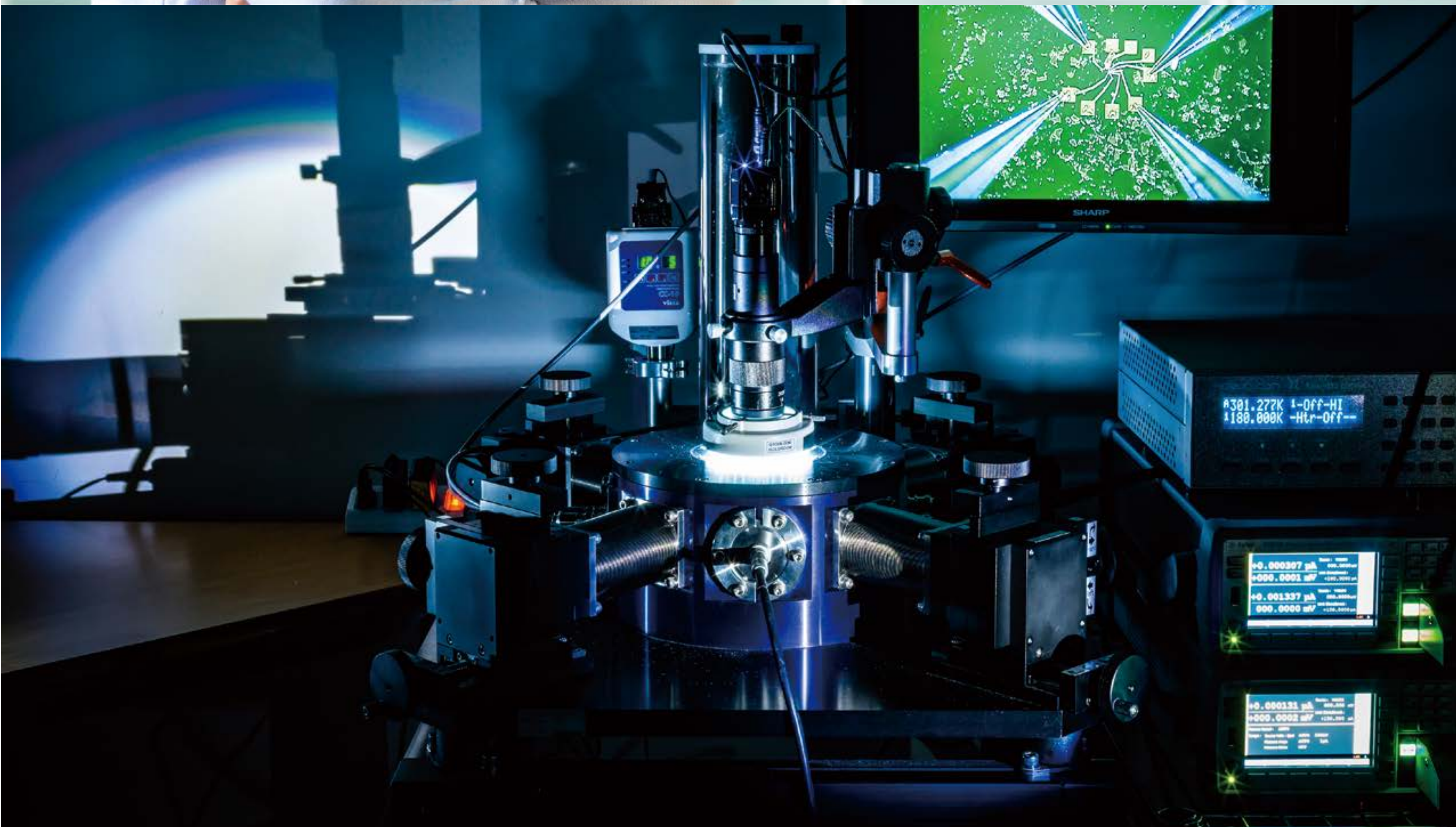
International Center for Materials Nanoarchitectonics (WPI-MANA)

Controlling nanoscale order

Architectonics connecting nanomaterials with macro materials



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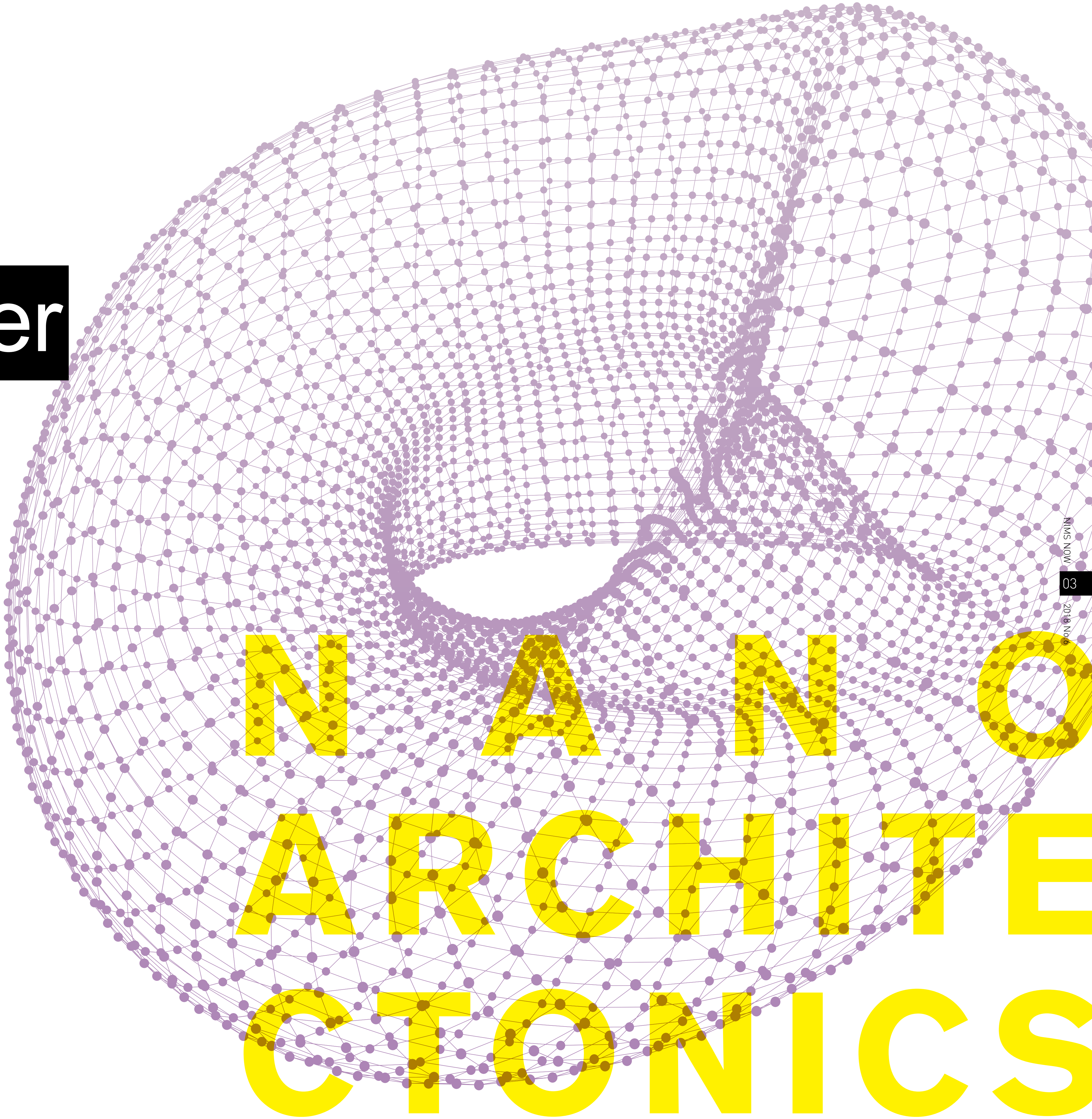
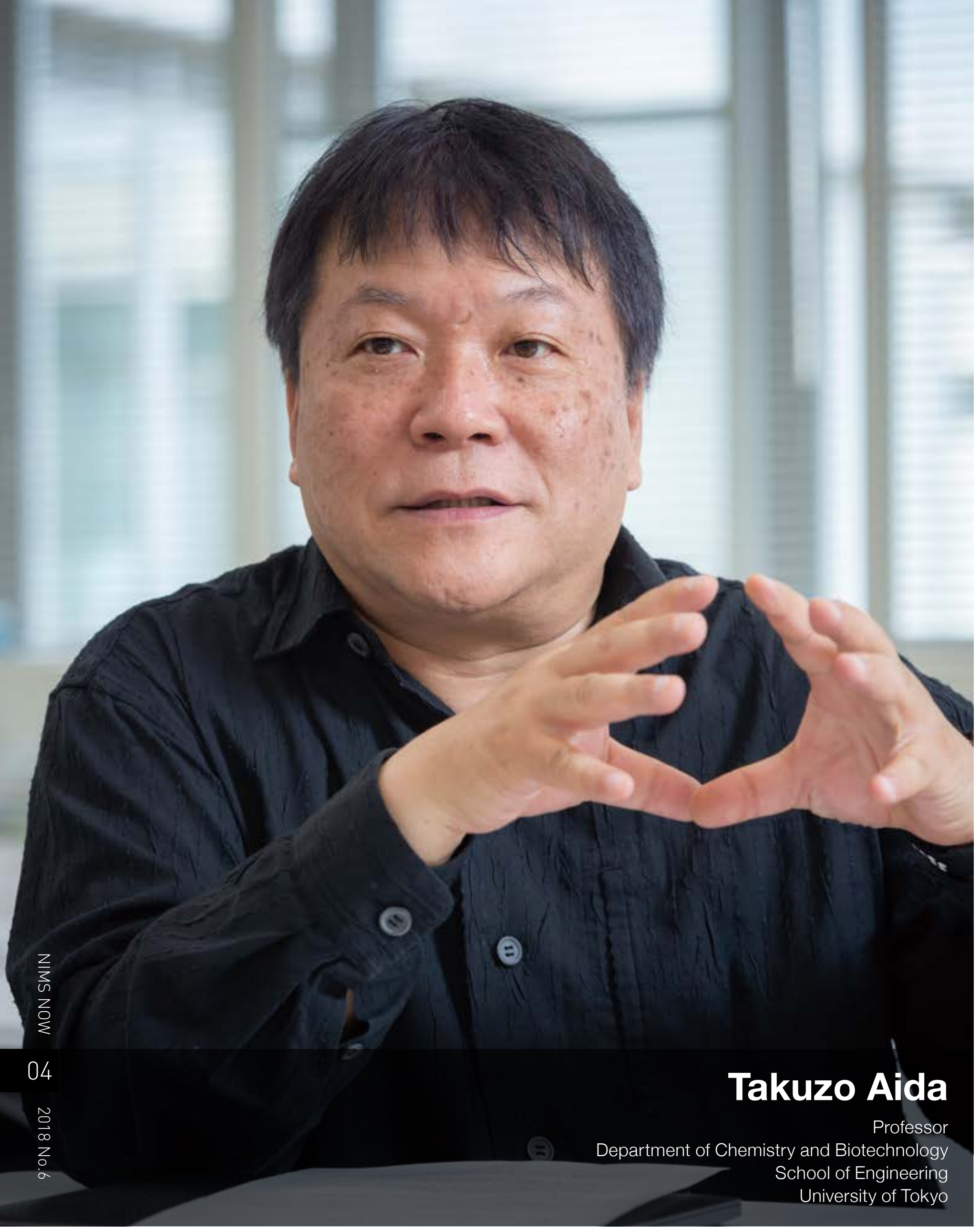
One-billionth-of-a-millimeter nanomaterials—atomic-scale in diameter and thickness
—come in a variety of forms, including nanoparticles, nanosheets and nanotubes.
Only close examination can reveal the unique, nanoscale-specific behavior of these materials.

The properties of nanomaterials have fascinated and inspired many scientists,
leading to rapid advances in nanotechnology.
The International Center for Materials Nanoarchitectonics (WPI-MANA)
was established in 2007 to accelerate nanotechnological research and development.
MANA has attained world-class status in the application of nanotechnology
to materials science as a result of implementing its 10-year plan.
Having made many significant research achievements,
MANA is now ready for even more advanced challenges.

MANA operates under solid guiding principles.
Its twofold mission is to create highly functional nanoarchitectures by actively assembling and
cross-linking nanomaterial components and to build novel physics knowledge through basic research.

Nanoscale order can be achieved in countless ways, e.g., by varying the combinations of or
stacking methods for nanomaterial components and by identifying unique and stable properties
using mathematical concepts.
The unknown nano-functions that await discovery are potentially as abundant as unknown nano-forms.





Takuzo Aida

Professor
Department of Chemistry and Biotechnology
School of Engineering
University of Tokyo

Special Talk

The growth of NANOARCHITECTONICS Research

Takayoshi Sasaki

Director
International Center for Materials Nanoarchitectonics (MANA)
National Institute for Materials Science (NIMS)

The NIMS International Center for Materials Nanoarchitectonics (MANA) was launched in 2007 with the support of the World Premier International Research Center Initiative (WPI Program) run by the Ministry of Education, Culture, Sports, Science and Technology. Takayoshi Sasaki became MANA's new Director in 2017 to continue to fulfill its mission. University of Tokyo Professor Takuzo Aida is a leader in polymer chemistry in Japan. Sasaki and Aida discussed the current status and future prospects of "nanoarchitectonics," a concept proposed by MANA.

Techniques to connect nanomaterials and macro materials

Sasaki: MANA is alone among NIMS' seven research centers and divisions specialized for basic research. "Nanoarchitectonics" is a concept proposed by MANA: creation of materials with novel functions by assembling or specifically organizing nano-sized materials (or nanomaterials).

Rapid progress of electronics and information/communication technology as well as the deteriorating environmental and energy situations have led to the growing demand for miniaturization, weight reduction and increased efficiency of various devices. Materials used in these technologies therefore need to be more compact, highly functional or multifunctional. I believe that basic research performed at MANA can greatly contribute to this endeavor.

Aida: Advances in nanoscience have made the fabrication of organic nanomaterials relatively easy. However, little attempt has been made to develop fundamental science to elaborate mesoscale structures: intermediate structures in scale between nano and macroscopic size regimes. A current challenge in polymer chemistry—my area of expertise—is the development of fundamental science to fill this missing link.

Sasaki: Nanomaterial research has evolved from the initial discovery of fullerenes and carbon nanotubes in the 1980s and 1990s to the development of nanomaterials in a wider range of compound classes, such as oxides, nitrides, metals and organics. In addition, active research efforts have been made on one-dimensional materials, such as carbon nanotubes, three-dimensional materials, such as nanoparticles, and then two-dimensional materials, such as graphene.

As you mentioned earlier, the most important and difficult challenges in nanoarchitectonics are the development of methods of synthesizing nanomaterials uniform in shape and size and of precisely organizing them. These challenges represent the essence of nanoarchitectonics. Addressing them could allow us to discover novel functions.

You developed a novel material containing titanium oxide nanosheets (see p. 12), a material I studied for many years. I think this exemplifies the practical application of nanoarchitectonic products.

Aida: I believe you are referring to a hydrogel, which was developed in 2015. This is a very unique material: this soft material is tolerant against a vertical compression force, but it deforms easily and drastically in response to a horizontal shear force.

This anisotropic hydrogel was derived from an "aqua material" developed in 2010. Although the water content of the aqua material is greater than 98%, it is very strong mechanically. The material can be readily prepared by mixing together natural clay mineral sheets and two types of polymers in water. Although the aqua material has many useful properties, I thought that an even more innovative material could be created by replacing the clay mineral sheets with titanium oxide nanosheets. This idea inspired me to engage in a joint research with Dr. Sasaki.

At that time, my lab had just acquired a superconducting magnet. A postdoctoral researcher in my lab used the magnet to apply a magnetic field to water containing titanium oxide nanosheets. As a result, all of the nanosheets neatly lined up in parallel in a direction perpendicular to the magnetic flux lines. Adjacent nanosheets were always separated by a gap due to mutual electrostatic repulsion. The researcher then allowed the nanosheet suspension to gelatinize in a manner similar to konjac jelly, resulting in the creation of a new anisotropic material (anisotropic hydrogel) in which the nanosheets are only allowed to slide horizontally. I think that this new material provides an excellent example to show what exciting things happen if the missing link between the nano and mesoscopic size regimes is filled.

Sasaki: After the development of anisotropic hydrogel, your lab's extremely talented researchers have produced a variety of new materials. All are very creative, including "photonic water" capable of changing color when the orientation of and intervals between nanosheets in water are altered by the application of an external force, such as heat.

Aida: Because researchers sometimes make discoveries by accident, I do not mind mistakes by researchers in my lab. When students conduct experiments and encounter unexpected results, I always encourage them to explore the possible causes of these results with curiosity.

Sasaki: I am deeply impressed with your work ethic. I believe that a sense of surprise serves as an important inspiration for scientists at research organizations, such as MANA, seeking to discover new materials, functions and phenomena. Surprise motivates us to create innovative materials. When we encounter unexpected or accidental events during our research, we should find them interesting and actively pursue their causes. An interdisciplinary approach to research is also important and our joint research really confirmed this point.

Aida: Basic research should always be a vigorous scientific activity, like producing something from scratch.

Power of computational science and human capabilities

Aida: I heard that NIMS actively integrates computational science into its efforts to find new materials. Has this approach been effective?

Sasaki: We consider computational science to be a very valuable means of obtaining certain types of information and insight that cannot be obtained solely experimentally. MANA was initially organized into two major research fields: the Nano-Materials Field and the Nano-System Field. A third field—the Nano-Theory Field—was newly added to MANA three years ago. It was arranged that a majority of the computational scientists at NIMS would join the Nano-Theory Field in an effort to integrate the theoretical and experimental approaches. Our method is to first make predictions regarding new materials and new physical properties using theoretical and computational approaches and then to verify these predictions experimentally. We hope this combined method produces many successes.

My hobby is to play the game of Go. I was overwhelmed by the news that a computer program, AlphaGo, had defeated a professional Go player. Relating this story to materials science, I hope that the use of computational science and machine learning will eventually lead us to make discoveries that are beyond our imagination.

Aida: My lab has integrated computational science into our research to a limited extent. For now, we use it only for the purpose of verifying the consistency of our experimental results theoretically. Although I ultimately want to increase the use of computational science in our pursuit of the discovery of new materials, I also want to continue to rely on human capabilities. Computer Go programs are certainly capable of advanced learning based on the rules of Go, but humans, as the inventers of Go, have immense creative abilities.

Basic research should be a vigorous scientific activity.

Takuzo Aida

For this reason, it is very important for us to train young researchers. We particularly need researchers capable of coming up with their own ideas and acting independently in order for Japan's materials science to remain strong in the future.

Sasaki: That issue needs to be addressed cooperatively between educational institutions—namely, universities—and national research institutions, such as NIMS and RIKEN. We are at a crossroads: we have to take appropriate action for Japan to maintain its scientific strength and remain attractive to scientists from all over the world.

The future of nanoarchitectonics

Aida: MANA's WPI Program has produced internationally recognized achievements in material-related nanotechnological research. I have had the opportunity to review many significant MANA accomplishments as a member of the MANA evaluation committee.

Sasaki: Thank you very much, Professor Aida. MANA currently has approximately 200 researchers, which represent about a quarter of the total number of NIMS researchers. MANA researchers engage in a wide variety of research. They fabricate various types of materials, such as nanowires, nanosheets, nanoporous materials and supramolecular materials, which may be applicable to next-generation electronics and energy technologies. In addition, they fabricate a large variety of different devices, from atomic switches to odor sensors.

MANA has also produced positive results in the development of nano-level analytical technologies. For example, MANA researchers combined a transmission electron microscope and a scanning probe microscope to enable simultaneous observation of a single nanomaterial at atomic resolution and measurement of its mechanical and electrical properties. The use of this technology has led to many unexpected discoveries.

When practical applicability is identified during basic research conducted at MANA, the subject matter is transferred from MANA to a NIMS mission-oriented research center to advance it to the applied research stage. Many of the researchers at the Center for Functional Sensors and Actuators, which was established in July 2018, were trained at MANA. This is a good example of MANA's contribution to NIMS as a whole.

Aida: Practical application of new materials takes 20 to 30 years after their discovery. It is important for future basic materials research to identify practical application potential. I look forward to continued outstanding work at MANA.

(by Kumi Yamada)

A sense of surprise motivates us to create innovative materials.

Takayoshi Sasaki

The growth of NANOARCHITECTONICS Research

Architectonics: Drawing blueprints

Topology: designing materials with a new language

Akihiro Tanaka
Group Leader,
Emergent Materials Property Theory Group,
Nano-Theory Field,
International Center for Materials Nanoarchitectonics (WPI-MANA)

Material properties are ultimately governed by the rules of quantum mechanics, which dictates the microscopic world consisting of arrays of atoms and a huge number of electrons swirling around them. A team of researchers led by Akihiro Tanaka is attempting to draw blueprints for materials exhibiting new functions, by looking into this quantum realm through the eyes of a new language – topology – and predicting their properties with the help of high precision numerical techniques.

Understanding materials through mathematics

“In 2016, a trio of scientists were awarded a Nobel Prize in physics for their ‘theoretical discoveries of topological phase transitions and topological phases of matter’,” Tanaka said. “After the award announcement, I did an interview on this subject with a reporter from a TV station. The opening question was: what is ‘topology’ ?”

Topology is a branch of mathematics which concerns itself with geometric properties that do not change when an object is gradually deformed; by the latter we mean that where topology is concerned, objects can be pulled or twisted, but cannot be ripped, cut, or glued together.

“Ideas having roots in topology began to enter into condensed matter physics in the 1980s,” Tanaka explains. “It started to dawn on physicists of that time that creating a state of matter which is in some sense topologically stable means it can persist even when perturbed by a fair dose of disorder such as crystalline defects, impurities, or thermal noise. In time, people realized that this unusual robustness could be turned into a huge advantage for designing material functions. Hence the enormous current focus on the subject.”

Here is a simple example — taken from everyday life as opposed to the quantum mechanical world of materials — of a topologically stable state. Imagine that you have a pole and a strip of rubber band. You wrap the rubber band around the pole once and then tie together the two ends. Notice that stretching or twisting the band does not change the number of times it has been wrapped around the pole. If you now want to wind the rubber band around the pole one more time, you first need to cut the band. If, alternatively you have wrapped the band around the pole twice and have tied the two ends, but now want to unwind it once, you again need to cut the band before you can do so. Thus, once the rubber band is tied around the pole, winding and unwinding require a major external change (i.e., cutting). This state —the number of wraps—is therefore said to be topologically stable.

Materials that are neither metals nor insulators

Incorporating topological ideas into condensed matter physics has led to the discovery of a number of topologically stable electronic states, which in turn give rise to extraordinarily stable materials properties.

The prototype example is the topological insulator, whose interior behaves as a metal, while its surface behaves as an insulator. Predicted theoretically in 2005, it was realized experimentally two years later.

“Topological insulators are unique in that they allow electric current to flow across their surfaces at a constant intensity virtually irrespective of their external environment,” Tanaka said. “Similar to the pole and rubber band example above, in which the number of wrappings is not easily changed, the conductivity at the surface of a topological insulator remains largely unchanged, being resilient to a considerable degree of perturbation.”

Tanaka continued, “One of our group’s goals is to follow in the footsteps of the discoverers of the topological insulator, and identify topological states of matter exhibiting new functions. For this purpose, let us recall that each electron is endowed with a spin —a tiny source of magnetism, in addition to its charge. If one finds a state where these tiny magnets are assembled into some nontrivial spatial pattern that is topologically stable, there is hope that a unique and extremely robust function is lurking within that material. Armed with this insight, members of our group undertook a theoretical investigation into the properties of GaV_4S_8, a magnetic insulator composed of gallium, vanadium and sulfur. This material had been reported to exhibit peculiar multiferroic properties and a topologically stable spin structure known as the skyrmion, but the precise relation between these two features was unknown.”

The search for new topological materials

The term multiferroics refers to materials that are simultaneously a magnet and a ferroelectric —the latter are materials which exhibit electric polarization in response to an applied electric field. This dichotomy allows magnetic (electric) properties to be controlled by an electric (magnetic) field in a multiferroic material, a feature which has a great potential for use in next-generation devices with a high energy efficiency.

Meanwhile, as depicted in Fig.1, the spins forming a skyrmion pattern point outward in a radial fashion. For this reason, it is sometimes also called a “hedgehog.” Skyrmions are known to be topologically stable; once formed, the pattern cannot disintegrate easily.

To investigate the relation between the occurrence of the mutiferroic feature and the formation of the skyrmion structure, Postdoctoral Researcher Sergey Nikolaev and Principal Researcher Igor Solovyev—both members of Tanaka’s research group—performed first principle calculations from which they extracted the magnetization distribution within GaV_4S_8 under the influence of an external magnetic field. They found that many skyrmions form into a lattice when GaV_4S_8 is exposed to a magnetic field whose intensity falls within a certain range (Figure 2).

Following this, the group evaluated the charge distribution pattern and established that these skyrmions are electrically polarized—negative charges were present at higher density in the inner region of the skyrmions than in the outer regions (Figure 3). This implies that a flow of mobile skyrmions will generate an electric current.

Tanaka explains: “In the absence of an external magnetic field, GaV_4S_8 is a featureless insulator. When subjected to a magnetic field of the right strength, some of the spins flip their orientations, leading to skyrmion formation. What people in our group demonstrated through their numerical study was that these skyrmions exhibit electric polarization and can serve as charge carriers. In other words, this work was the first to show explicitly that for a certain range of magnetic field strength, skyrmions are the source of the multiferroic function of GaV_4S_8. Tanaka surmises that the mechanism found may lead to a novel charge transport application, where the lattice of skyrmions migrates in response to an electric or magnetic field.

In many of the topological materials known to date, it is the correlation among electrons from which exotic properties very different from those of the individual electrons emerge. Tanaka, using an analogy to this aspect, remarks: “We are a group of researchers with a considerably diverse background. As such, I am hoping that the correlation among members will result in the discovery of materials with exciting new functions.”

(by Shino Suzuki, PhotonCreate)

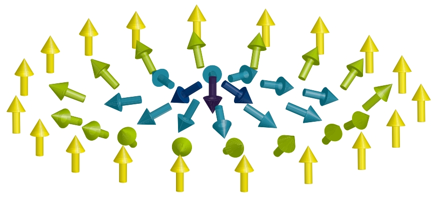


Figure 1. Skyrmion spin structure

A skyrmion is composed of radially aligned spins. The outer spins point upward while the inner spins point downward. As a whole, the spins point in all possible directions exactly once. In precise analogy to the pole and rubber band example discussed in the text, this number cannot change continuously; changing it will be energetically costly. Once formed, skyrmions are therefore stable and will not readily decay.

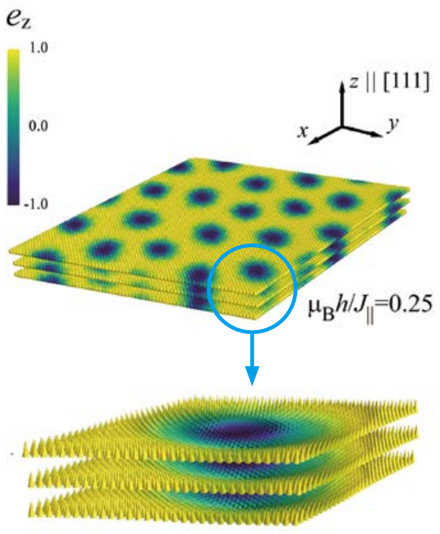


Figure 2. Formation of magnetic skyrmions in GaV_4S_8 under an applied magnetic field

In GaV_4S_8, a layered material, skyrmions form a lattice pattern on each layer.

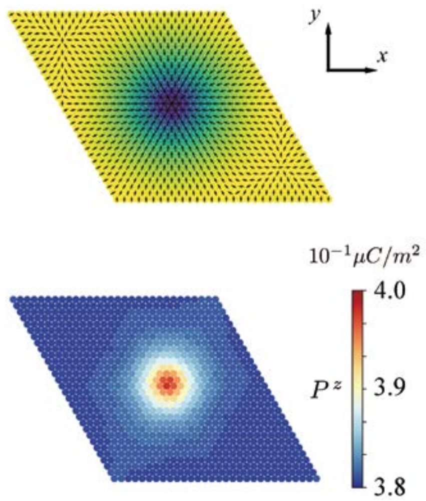


Figure 3. Magnetization distribution (top) and electric polarization (bottom) in a GaV_4S_8 layer

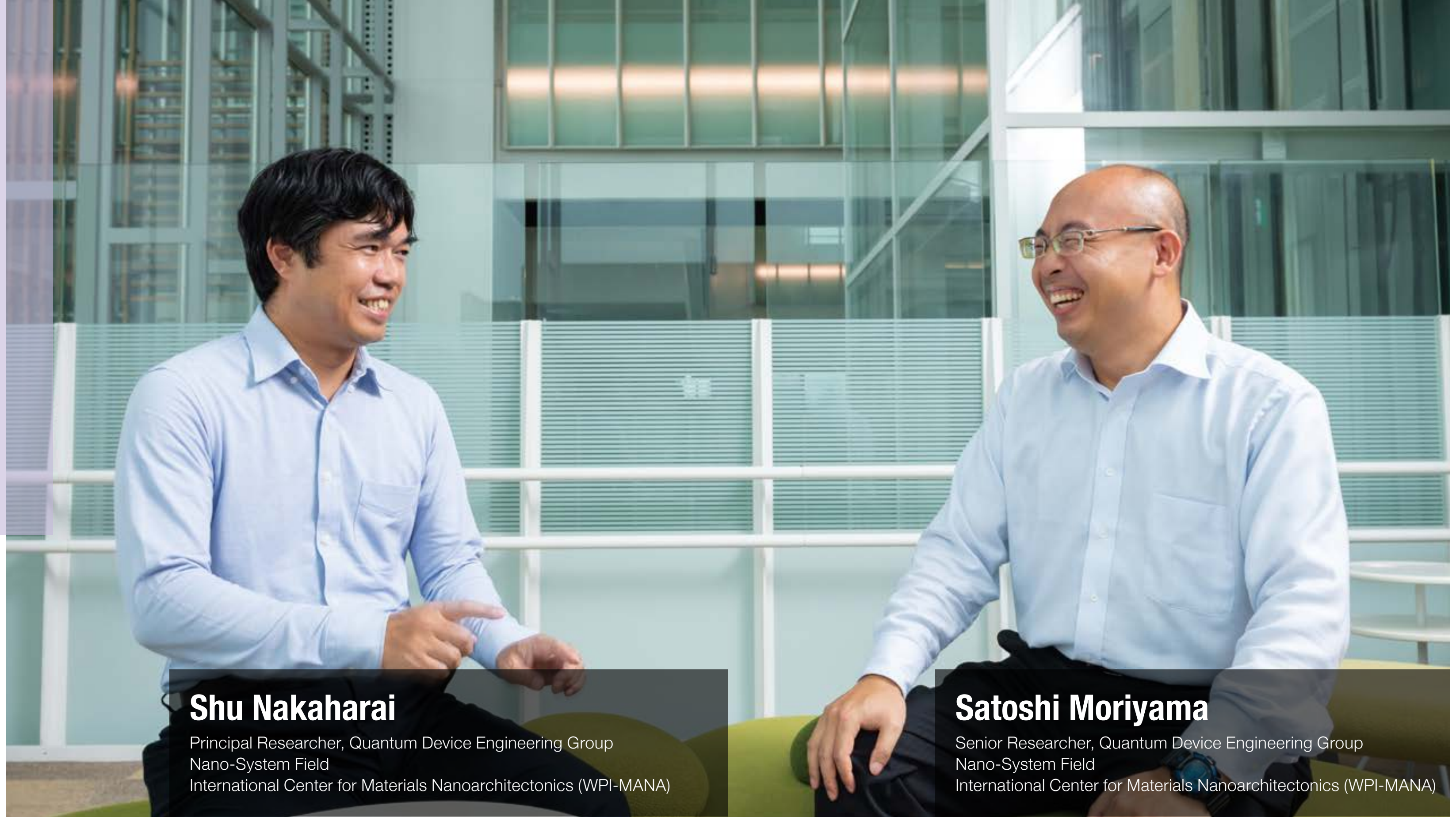
Electric polarization in a skyrmion causes negative charges to be present at higher densities in the inner region than in the outer region.

Sergey Nikolaev and I. Solovyev, arXiv: 1808.08008

Architectonics: Extracting hidden functions

Searching for functions woven into sheet material

Two-dimensional sheet materials are only one to several atoms in thickness. When different types of sheet materials are stacked, the combination may exhibit properties different from those of the individual monolayers. Multiple layers of the same sheet material may also show different properties depending on the number of layers stacked and the angular differences between the layers. Shu Nakaharai and Satoshi Moriyama have been searching for new functions and physics hidden in these layered structures.



Shu Nakaharai
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Dawn of the exploration of two-dimensional materials

Imagine that you have a graphite block. You attach adhesive tape to the block and peel it to remove the surface layers. You then attach another piece of tape to the removed surface layers for further peeling. If you repeat this process over and over, you eventually obtain a single-atom-thick graphite or graphene sheet. Graphene has driven two-dimensional material research.

Graphene is composed of carbon atoms arranged in a honeycomb pattern. Due to its unique properties—it is strong yet flexible and highly conductive electrically and thermally—graphene is potentially useful for a variety of purposes. "Graphene may be applicable to transistors—semiconductor devices that control the flow of electric current in electronic circuits," Nakaharai said. "Most transistors today are made from silicon. If graphene, a thin material with high charge mobility (i.e., high electrical conductivity), can replace silicon, highly integrated and power-efficient transistors may be developed."

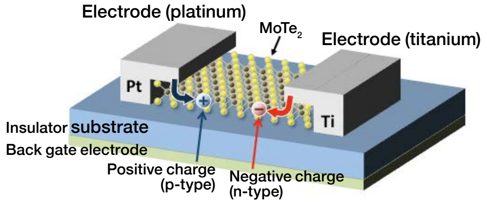

Figure 1. $MoTe_2$ transistor structure

$MoTe_2$ exhibits both p- and n-type behaviors by accepting both positively charged holes from the platinum electrode and negatively charged electrons from the titanium electrode, respectively.

Advent of a predecessor to graphene

When graphene first became available, it attracted Nakaharai's attention; he was then developing transistors at an electronics manufacturer. However, he found that its usefulness in transistors was limited because highly conductive graphene was to be used as a semiconductor. "I discovered that graphene can be used as a semiconductor by irradiating it with helium ions, thereby creating defects in its crystalline structure," Nakaharai said. "However, this treatment also caused graphene's charge mobility to decrease, undermining its advantages."

While struggling with this issue, Nakaharai saw an intriguing report about a group of materials called transition metal dichalcogenides (TMDCs) which are composed of multiple stacked sheets made of transition metals and chalcogens. He learned that individual TMDC layers can be isolated using adhesive tape in a manner similar to graphite layers. "Each TMDC sheet is several atoms in thickness and behaves as a semiconductor," Nakaharai said. "I later transferred to NIMS and began studying the use of TMDCs in transistors."

However, Nakaharai had to deal with yet another issue. Transistors have two types of p- and n-types, and both need to be incorporated into an integrated circuit. However, it was difficult to control the transistor type between p- and n-types in TMDCs.

TMDC properties vary greatly depending on the combinations of transition metals and chalcogens. While studying these combinations, Nakaharai found molybdenum ditelluride ($MoTe_2$) to be promising. "$MoTe_2$ had been researched only to a limited extent because it is difficult to deal with," Nakaharai said. "However, when high-quality single-crystalline $MoTe_2$ became available, I selected it as my research focus in the hope of discovering interesting physics."

Nakaharai focused on a Schottky barrier formed at the junction between a metallic electrode and a semiconductor. This barrier blocks the flow of electrons and holes. Nakaharai found that the Schottky barriers formed in $MoTe_2$ were more easily removable than those formed in other TMDCs, such as molybdenum disulfide. If the Schottky barriers are removed, electrons and holes can be injected from the metal electrodes into $MoTe_2$, which potentially allows controlling the transistor type of p- and n-types. After examining combinations of $MoTe_2$ with various metals, Nakaharai discovered in 2015 that $MoTe_2$ displays p-type behavior in combination with platinum and n-type behavior in combination with titanium (Figure 1). Thus, he has come one step closer to achieving the use of two-dimensional materials in transistors. In addition to these efforts, Nakaharai has also been attempting to use graphene and TMDCs in sensors.

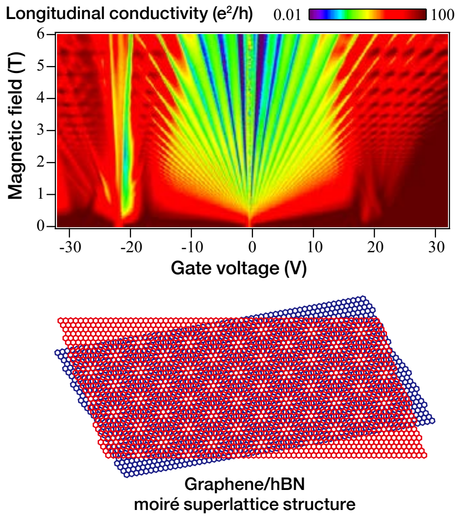

Figure 3. "Butterfly" that describes both the quantum Hall effect and moiré superlattice structures

(Top) A color scale plot descibing electrical conductivity (longitudinal conductivity in e^2/h, where e and h denote elementary charge and the Planck constant, respectively) as a function of the gate voltage and the magentic field applied perpendicular to the graphene sheet. The pattern shown, called a "Hofstadter's butterfly," indicates that electrical conductivity is high and the angular difference between the two stacked honeycomb structuers is 1° degree or less. (Bottom) A schematic diagram of a moiré superlattice structure. For better visibility, an angular difference of 10° between the two sheets is shown.

Stacking two types of honeycomb structures

"Another fascinating aspect of two-dimensional materials is that they exhibit new properties when stacked," said Moriyama, who fabricated a device composed of stacked sheets of graphene and hexagonal boron nitride (hBN) to which electrodes were attached at opposite ends (Figure 2). hBN is a material composed of boron and nitrogen atoms arranged in a honeycomb pattern. Very high quality crystalline hBN was fabricated and provided to Moriyama by Research Fellow Takashi Taniguchi and Chief Researcher Kenji Watanabe at NIMS.

Electrical conductivity measurement results confirmed that the charge mobility of Moriyama's device was among the highest in the world and that a unique phenomenon called the quantum Hall effect occurred in the device. In addition, analysis of measurement data revealed that a moiré superlattice structure was formed when the angular difference between the two stacked honeycomb structures was 1° or less (Figure 3).

"'Valley current' had been predicted to occur in materials with moiré superlattice structures," Moriyama said. Electrons in solid crystals have hidden degrees of freedom, called valley degrees of freedom, in addition to charge and spin degrees of freedom. "Valleytronics"—the use of valley current to transmit information without the involvement of charge current—has the potential to lead to the development of highly energy efficient electronics. However, previous valleytronics research had detected only very weak signals inappropriate for practical application.

Moriyama converted electrical signals in the device he fabricated into valley currents. He then converted the valley currents back into electrical signals, which enabled him to successfully detect the substantial electrical signals indicative of valley current. Fabrication of the high-quality device made this accomplishment possible. "I believe that the valley current we detected recently was actually quantum valley current, although this still needs to be verified," Moriyama said. "I expect that our first-in-the-world observation of quantum valley current will allow quantum computing devices to be more widely applied."

An American research group recently reported that stacking two graphene layers with an angular difference of 1.1° between them induces superconductivity in the stacked material.

"Two-dimensional materials can be combined in myriad ways by changing the number of stacked layers and the angular difference between the layers," Moriyama said. "These experiments stimulate my imagination because manipulation of these combinations may lead to the discovery of novel functions." Nakaharai also shared his goals going forward. "I hope to continue investigating the functions and physics of two-dimensional materials in the hope of contributing to the development of next-generation electronics."

(by Shino Suzuki, PhotonCreate)

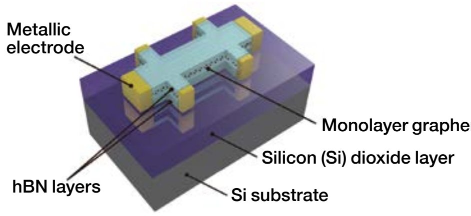

Figure 2. Graphene superlattice device

Graphene was placed on top of an hBN layer. Another hBN layer was then placed on top of the graphene to prevent contamination. Finally, electrodes to measure electrical conductivity were attached to the stacked layers.

S. Nakaharai, et al., ACS Applied Materials & Interfaces 8, 14732-14739 (2016). DOI: 10.1021/acsami.6b02036
K. Komatsu et al., Science Advances 4, eaaq0194 (2018). DOI: 10.1126/sciadv.aaq0194

Architectonics: Assembling Nanosheets

Constructing highly functional materials by assembling nanosheets like “mille-feuille” layers

Renzhi Ma
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Functional Nanomaterials Group
Nano-Materials Field
International Center for Materials Nanoarchitectonics (WPI-MANA)

Some layered materials are difficult to separate into individual layers due to the strong bonds between them. Renzhi Ma and colleagues at MANA have developed chemical techniques to easily separate these layers. In addition, they are able to assemble many different types of single-molecule-thick sheet materials in a designated order. Artificial composite materials synthesized according to blueprints may exhibit unique functions different from those of homogeneous materials.

Exceptional layer separation and assembling techniques

As Ma swirled a liquid in a flask, tiny materials in the liquid reflected light in random directions. These are nanosheets—ultimately thin two-dimensional materials one to several atoms in thickness and more than several thousand atoms in width with unique nanoscale properties.

In nature, single-sheet materials rarely exist; they normally exist as multilayered solids (layered materials). If the individual layers in layered materials are held together by weak bonds, they can be separated using adhesive tape. However, if they are held together by strong bonds, this method may not be feasible.

MANA has developed the world’s first technique that can effectively separate layered materials into individual nanosheet components. Optimum nanosheet separation techniques are available for various materials, including oxides (e.g., titanium dioxide [TiO_2] and manganese dioxide [MnO_2]) and hydroxides containing transition metals or rare earth elements.

MANA has also developed its original techniques for use in fabricating artificial lattice materials composed of different types of assembled nanosheets. These techniques may enable breakthroughs to be made in the development of various devices, such as the world’s smallest, high-performance capacitors, electrochemical supercapacitors capable of quickly storing and releasing large amounts of electrical energy within tens of seconds and extremely high efficiency electrode catalysts free of platinum and other precious metals.

Development of energy materials through skillful design and control

Artificial lattice materials composed of assembled nanosheets have many potential applications. Ma’s group has been focusing on their use as rechargeable battery materials. The capacity of the rechargeable batteries currently used in electric vehicles is insufficient in terms of mileage per charge. The development of higher-capacity batteries is therefore indispensable. In addition, new batteries will be required to have extended cycle lives; i.e., increased endurance to the deterioration caused by repeated charge and discharge.

Lithium ion batteries—the most widespread rechargeable batteries in current use—are composed of an electrolyte, cathode and anode. The capacity of rechargeable batteries is influenced by the properties and combinations of battery materials used. Ma’s group recently worked to increase anode capacity using MnO_2 as an alternative to the carbon anode materials in current use. The theoretical capacity of MnO_2 is at least three times higher than that of carbon materials. If MnO_2 were separated into individual one-molecule-thick monolayers, the reaction efficiency was expected to increase when used as an anode material, because the MnO_2 surface area exposed to an electrolyte was increased.

The high theoretical capacity of MnO_2 is attributed to its tendency to be reduced from MnO_2 to Mn by releasing oxygen ions. However, the release of oxygen ions damage the MnO_2 crystalline structure. Only two or three charge/discharge cycles may severely damage the crystalline structure and significantly reduce its capacity. Separate MnO_2 monolayers are even more fragile and tend to clump together. Thus, high-capacity MnO_2 nanosheets are facing the issue of a short cycle life.

Ma’s group attempted to resolve this issue using graphene (a sheet material composed of carbon atoms arranged in a honeycomb pattern). The group initially proposed that a crystalline structure composed of assembled alternating MnO_2 and graphene nanosheets—which resembles mille-feuille in appearance—would not collapse (though it might deform) and would not clump together when oxygen ions are released.

However, the group encountered difficulties when implementing the planned alternating assembling. The group was able to synthesize large quantities of graphene at low cost by subjecting graphite to a chemical oxidation treatment and separating it into nanosheets. However, this treatment generated defects in the synthesized graphene nanosheets, altering their properties. The group thus treated the graphene nanosheets with electron donors to induce reduction reactions, repairing the defects and restoring the properties of the nanosheets to a satisfactory level. The resulting reduced graphene oxide (rGO) nanosheets, however, had negatively charged surfaces which repelled similarly negatively charged MnO_2 nanosheets, making alternating assembling impossible. To address this issue, the group developed a process to attach PDDA polymers to rGO nanosheets, resulting in the production of positively charged, PDDA-modified rGO nanosheets which are attracted to negatively charged MnO_2 nanosheets (Figure 1).

Drop-by-drop addition of graphene to MnO_2 nanosheets in an Erlenmeyer flask while it is being stirred yields self-assembly of composite materials consisting of alternating assemblings of MnO_2 and graphene nanosheets. “This procedure does not have to be carried out at high temperature or high pressure,” Ma said. “Although this manufacturing technique does not allow precise control of the number of layers assembled, it enabled us to produce composite materials consisting of approximately five to 20 layers (Figure 2).”

Ma’s group evaluated the composite material for its usefulness in electrodes and found that it can serve as a high-capacity, long-life anode material when MnO_2 and graphene nanosheets are present in a 1:1 ratio by area. Its anode capacity was at least twice that of commercial lithium ion batteries, while its capacity decay per cycle was only 0.004% after 5,000 charge/discharge cycles.

Expanding the applications of nanosheets

“We had another reason for using graphene,” Ma said. “In conventional rechargeable batteries, MnO_2 electrodes are supplemented with electrically conductive fine carbon particles in order to facilitate the movement of electrons into and out of the electrodes. I assumed that graphene could perform the same function as these conductive fine carbon particles if used in a battery system and I was very happy to find that batteries with graphene perform outstandingly—the performance values we obtained were superior to those reported previously using other metal oxide anode materials. We have also been developing supercapacitors and electrode catalysts. If all of these technologies are put into practical use, we should be able to dramatically increase energy storage efficiency.”

Other nanosheet assembling techniques are also available that allow gradual, sheet-by-sheet stacking. “The use of these techniques enables precise control of nanosheet assembling in terms of layering order and the number of layers, like stacking Lego blocks,” Ma said. “There are countless combinations in nanosheet assembling. In future research, we will apply these techniques not only to the development of electrode materials but also to the development of other functional materials.”

(by Kaori Oishi)

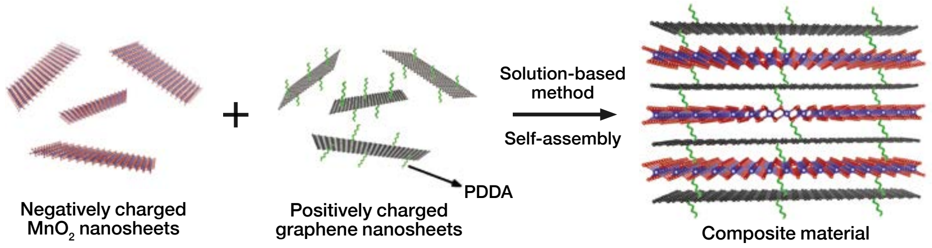

Figure 1. Mechanism of alternately assembling MnO_2 nanosheets and graphene nanosheets
Positively charged graphene nanosheets are prepared by allowing PDDA (poly [diallyldimethylammonium chloride]) polymers to attach to reduced graphene oxide (rGO) nanosheets. Positively charged graphene nanosheets and negatively charged MnO_2 nanosheets can be assembled alternately by simply mixing and lightly stirring the solutions.

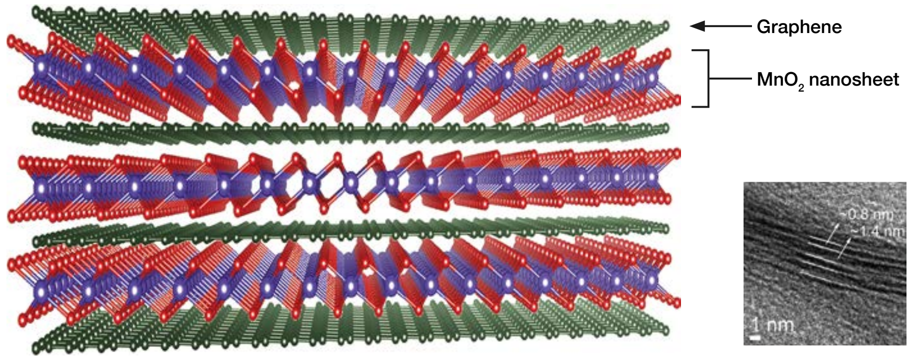

Figure 2. Anode material composed of assembled alternating MnO_2 nanosheets and graphene nanosheets
MnO_2 nanosheets are 0.8 nm in thickness while PDDA-modified reduced graphene oxide (rGO) nanosheets are 1.4 nm in thickness. A transmission electron micrograph of the layered structure is shown on the right. Ma said, “The anode capacity of this material at its current density of 0.1 A/g is 1,325 mAh/g. Its cycle life has been greatly increased.”

Ma & Sasaki, Accounts of Chemical Research 48, 136-143 (2015). DOI: 10.1021/ar500311w
Xiong et al,. ACS Nano 12, 1768-1777(2018). DOI: 10.1021/acsnano.7b08522

TOPIC

Launch of L'Oréal-NIMS Materials Innovation Center for Science and Beauty

Smart beauty polymers

NIMS established a joint research center in July 2018 with Nihon L'Oréal K.K., the Japanese subsidiary of the world's largest cosmetics company, L'Oréal S.A. Nihon L'Oréal has identified "smart polymers" to be potentially applicable to cosmetics. The properties of smart polymers are capable of changing in response to external stimuli, such as ultraviolet light, temperature and humidity. Use of these materials may allow development of next-generation "smart" cosmetics.

Mitsuhiro Ebara

Co-Director of the L'Oréal-NIMS Materials Innovation Center for Science and Beauty; MANA Associate Principal Investigator, Mechanobiology Group, International Center for Materials Nanoarchitectonics (WPI-MANA), NIMS

Smart polymers are easily controllable materials whose properties can be changed or restored by external stimuli. For example, some smart polymers that have been stretched are able to instantly return to their original shapes when placed in hot water. It is difficult to change the properties of most polymers; most need to be changed its chemical structure by mixing with chemicals in a reaction tank. The properties of smart polymers, by contrast, can be readily changed by certain ultraviolet, humidity, temperature or pH conditions. "Polymers synthesized by precisely combining and sequencing molecules can exhibit various functions," Mitsuhiro Ebara said. "For example, you can change the transparency and water repellency of these polymers by exposing them to certain types of stimuli. Smart polymers have great potential as functional materials. In addition, the shapes of smart polymers that have been processed into films, gels or liquids, etc. can be designed as needed. Because they are inexpensive, they can be used even as advanced medical materials for people in developing countries and disaster-affected areas." These useful smart polymers are also potentially applicable to cosmetics.

Nihon L'Oréal and NIMS jointly founded the Materials Innovation Center for Science and Beauty in July 2018. They plan to develop versatile products that will satisfy various needs, such as shape-memory hair styling products and anti-wrinkle, anti-sag skincare products, in relation to country-specific consumer needs and social situations.

"MANA's resources are ideal for the production of new nanomaterials," said Ebara. "I have been striving to establish polymer synthesis techniques that will enable precise molecular design faithful to the original blueprints based on the nanoarchitectonics concept. MANA has many experts in various fields who share this concept. I enjoy the opportunity to consult with analytical specialists about methods of evaluating synthesized polymers, which sometimes leads to the assembly of original analytical devices," Ebara said proudly. Nihon L'Oréal has all of the infrastructure necessary to speedily commercialize cosmetic products, including cosmetic scientists and product testing facilities.

Ebara previously devoted his efforts to applied research on medical products. "I have been researching smart polymer sheets that can be attached directly to cancer cells as a cancer treatment with the goal of saving as many lives as possible. Although beauty care research does not affect people's lives as directly, it can improve quality of life. This collaboration opportunity has broadened my perspective. In the future I will strive to develop products that will bring smiles to people's faces."

(by Kaori Oishi)

L'Oréal's mission is to "provide the best in cosmetics innovation to women and men around the world while respecting their diversity." NIMS—a world-class materials research institute that has put a number of technologies into practical use in collaboration with various industries—is an indispensable partner that can help us to fulfill this mission. Our initial goal in this partnership is to develop commercial products using smart polymers—very promising materials that may enable us to put innovative cosmetics concepts into practice. At the Materials Innovation Center for Science and Beauty, we intend to combine materials science and cosmetic science to formulate unique ideas and develop new materials capable of meeting consumers' beauty care needs. We hope to bring innovation to the world of cosmetics by introducing materials developed through our collaboration with NIMS to L'Oréal products.

Jun Sasai

Co-director of the L'Oréal-NIMS Materials Innovation Center for Science and Beauty, Nihon L'Oréal K.K.

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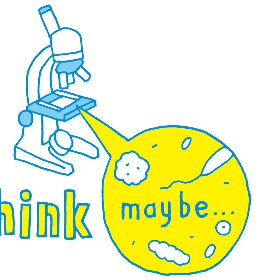
Science is even more amazing than you think



Microorganisms that produce nanomagnets

Text by Akio Etori

Illustration by Joe Okada (vision track)

Countless microorganisms are living and moving around us every day. They are several microns in size and are, of course, invisible to the naked human eye (as are all objects smaller than approximately 0.1 mm or 100 microns).

According to some estimates, the total animal biomass of the earth amounts to several billion tons, while total plant biomass amounts to from one to two trillion tons. The total biomass of microorganisms, by comparison, is estimated to amount to 200 to 300 billion tons. It has been theorized that underground-dwelling microorganisms will add greatly to this figure.

About 100 trillion microorganisms are estimated to exist in a single human body. Our intestines are known to contain particularly large amounts of microorganisms, including about 1.5 kg of intestinal bacteria.

Humankind has been taking advantage of some microorganisms since ancient times, such as yeasts to make bread, the koji fungus to make miso and certain bacteria to make yogurt.

The invention of microscopes enabled scientists to begin to understand microbial activity, which led to a wider range of microbial applications. Antibiotics, including penicillin, have been used medically to suppress disease-causing microorganisms and have saved many lives.

Although we closely interact with microorganisms throughout our lives, humans have so far identified only a fraction of the microbial species in existence. For example, ivermectin, an important life-saving medication developed by 2015 Nobel Prize winner Satoshi Ōmura, was derived from a new microbial species isolated from soil samples collected from various locations. This indicates that unknown microbial species living in our habitats have the potential to bring great benefits to our lives.

So-called "magnetic bacteria" inhabit various aquatic environments around the world, such as ponds, marshes and lakes. They are currently attracting a great deal of attention for their ability to produce tiny magnets within themselves.

The most widely accepted theory holds that these bacteria produce magnets for migration purposes. The earth acts as a giant magnet, with its magnetic north pointing to geographic south and its magnetic south pointing to geographic north. The earth's rotational axis is tilted from the ecliptic plane. Magnetic bacteria are thought to use their internal magnets like compasses to navigate northward (if they are in the Northern Hemisphere) or southward (if they are in the Southern Hemisphere) in search of more suitable water bottom habitats.

Magnetic bacteria ingest iron ions and use them to synthesize fine magnetic particles of magnetite (Fe_3O_4). These bacteria may be used to efficiently produce great quantities of nanomagnets without large equipment—an appealing idea in various industries seeking to introduce microbial technologies. I have learned that international scientific meetings are now being held specifically to discuss magnetic bacteria and that magnetic bacteria are the subject of active research, from basic science to industrial applications.

Proteins (enzymes) involved in the synthesis of fine magnetic particles were recently discovered, and mechanisms that control the crystalline structures of these particles have been identified. In addition, Tokyo University of Agriculture and Technology has reportedly succeeded in sequencing magnetic bacterial genomes for the first time and has identified a gene set common to all magnet-producing microorganisms.

If the engineering of magnetic bacterial genes enables controlled synthesis of nanomagnets in various forms, I would expect wide-ranging demand for them. I also believe that magnetic bacteria have great potential for use in drug delivery systems in which the bacteria could be manipulated to ingest drugs to be delivered and guided to a target site through the application of an external magnetic force.

I have no doubt that humans will continue to heavily rely on microorganisms.

Akio Etori: Born in 1934. Science journalist. After graduating from College of Arts and Sciences, the University of Tokyo, he produced mainly science programs as a television producer and director at Nihon Educational Television (current TV Asahi) and TV Tokyo, after which he became the editor in chief of the science magazine Nikkei Science. Successively he held posts including director of Nikkei Science Inc., executive director of Mita Press Inc., visiting professor of the Research Center for Advanced Science and Technology, the University of Tokyo, and director of the Japan Science Foundation.

MANA INTERNATIONAL SYMPOSIUM 2019 Jointly with ICYS

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Time and date: **March 4-6, 2019**
Banquet: March 5, 18:30-20:30

Venue: **Tsukuba International Congress Center EPOCHAL TSUKUBA**

Symposium Registration Fee: **free** / Banquet Participation Fee: 3,000yen, 1,500yen (student)

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Requires Online-Registration prior to February 25, 2019. Please access the following web site.

http://www.nims.go.jp/mana/2019/index.html

The International Center for Materials Nanoarchitectonics (WPI-MANA) is attempting to create a new paradigm for materials science, called “nanoarchitectonics”, based on an innovative nanotechnology. WPI-MANA has held the MANA International Symposium every year to discuss the current status and the future perspective of materials science based on the state-of-the-art nanotechnology together with many distinguished scientists and young scientists from around the world.

In the 12th MANA International Symposium (jointly with ICYS: International Center for Young Scientists), we design the symposium to initiate discussion about “Nano Perceptive Materials, Devices, and Systems”. In addition to guest lectures renowned nanotechnology and material science achievements in relevant research fields, the researchers from MANA and ICYS will present their latest findings for extensive discussion for future.

We hope many scientists, researchers and students who are interested in materials science and technology will join this symposium and obtain fresh inspiration from the talks and discussions towards the future.

Keynote Speakers

Prof. DECHER, Gero (University of Strasbourg, France)
“Bioinspired nano-composite materials with complex anisotropies”

Prof. IWASA, Yoshihiro (The University of Tokyo, Japan)
“Emergent Iontronics”

Prof. MALLOUK, Thomas E. (The Pennsylvania State University, USA)
“How Do You Make a Micro-Robot?”

※All lectures will be conducted in English.
※Programs are subject to change without notice.

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