NATIONAL INSTITUTE FOR MATERIALS SCIENCE

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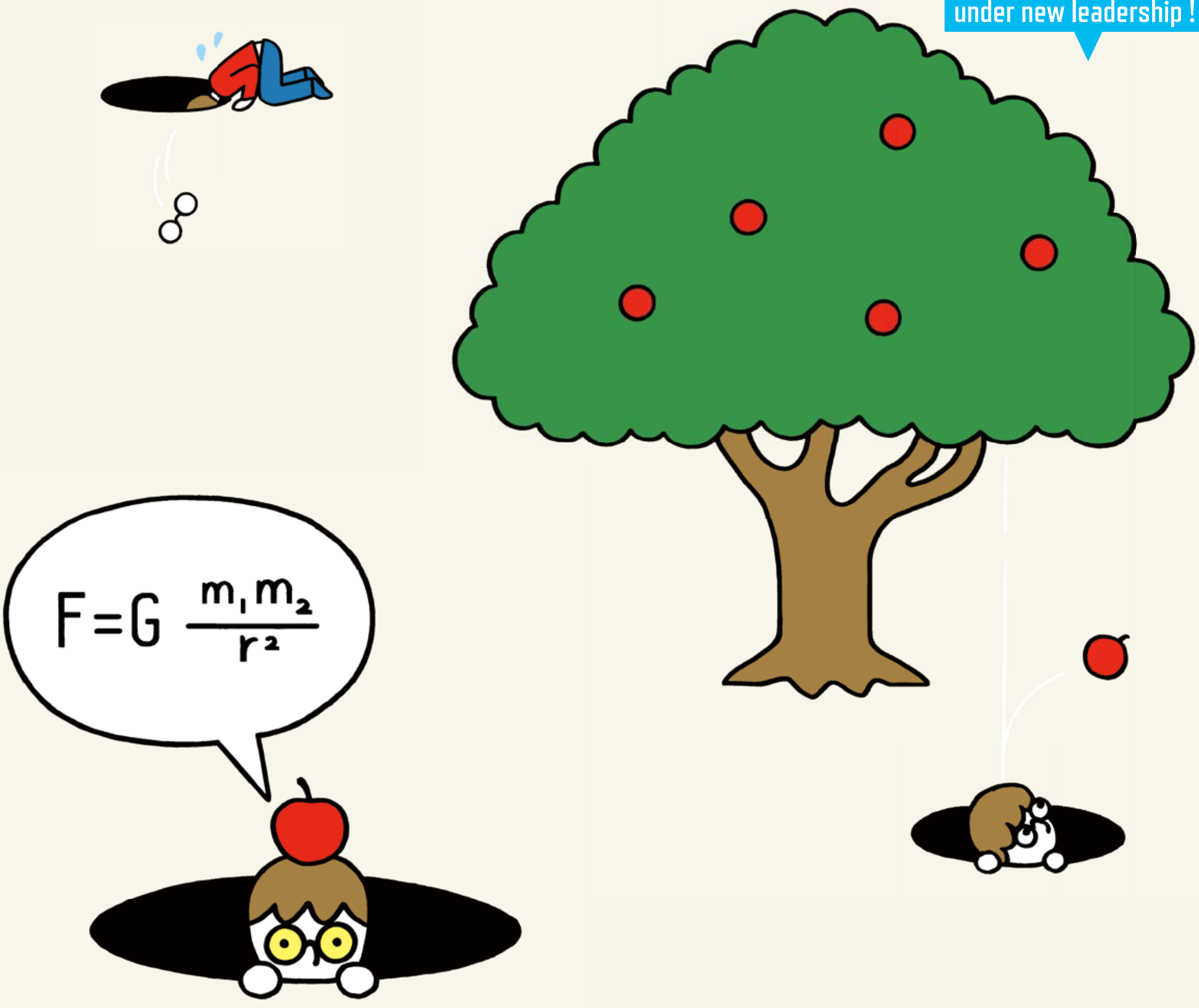
NIMS makes a fresh start under new leadership !



THE ECCENTRIC VIEWS OF MATERIALS SCIENTISTS

NIMS makes a fresh start under new leadership

Kazuhiro Hono

President, National Institute for Materials Science (NIMS)

As of April 1, 2022, I have been appointed as the fourth President of the National Institute for Materials Science (NIMS). Previously, the presidents of NIMS had been selected from a pool of distinguished scientists with strong management experience from other research institutes. For the first time, a researcher with a major career at NIMS assumes the position of the president. So, I feel that the weight of this responsibility is on me.

When I moved from a university to the National Research Institute for Metals (NRIM), the predecessor of NIMS, in 1995, I was surprised to find many restrictions on collaborating with companies, obtaining external funds, making business trips, hiring post-docs, etc. In 2001, NIMS was incorporated as an independent administrative institution together with the National Institute for Research in Inorganic Materials (NIRIM), and the first president, Professor Teruo Kishi, made major reforms to create an environment in which NIMS researchers can devote themselves to research with a great degree of freedom and discretion. At the same time, the researchers were exposed to a competitive environment with universities and other research institutes, and it became important for individual researchers to be highly esteemed externally. The adoption of MANA (International Center for Materials Nanoarchitectonics) as a World Premier International Research Center (WPI) program in 2007 was the most symbolic event representing the changes after NIMS became an independent administrative institution. In addition, the International Center for Young Scientists (ICYS) was established, attracting many talented researchers from around the world, some of whom have now become members of the permanent research staff at NIMS. Under the leadership of the second President, Professor Sukekatsu Ushioda, the internationalization of NIMS was further promoted, and the global presence of NIMS in the field of materials science has increased.

Under the leadership of the third President, Professor Kazuhito Hashimoto, who took office in 2016, NIMS was transformed into one of three Designated National Research and Development Institutes and its mission was defined to make contributions to the society by creating world-class research achievements based on national strategies. In addition to the mission-oriented research, President Hashimoto strongly supported bottom-up fundamental research that is proposed based on individuals' free ideas, and as an organizational effort, the energy and environmental materials and data-driven research was strongly supported. Other new measures included the establishment of Materials Open Platforms (MOPs) in various fields of materials engineering, the promotion of the exchange of university faculty and graduate students, and the support to start-up companies. I have participated in the management of NIMS for the past four years under the leadership of former President Hashimoto, and I will do my best to continue working on these measures.

Another important issue that I will tackle as the fourth President of NIMS is to recruit excellent researchers to strengthen the global competitiveness of NIMS in the materials science field even further. According to the number of citations of papers in the field of materials science, NIMS has maintained the top position in Japan since 2012, but its global rankings has been declining year by year. This is a common trend not only in materials science but in general in Japanese science and technology, but for Japan, which has strong materials industry, the decline in the global position of fundamental research in materials science is a worrisome issue. NIMS is committed to creating an excellent research environment where scientists can devote themselves to research, so we have been able to attract excellent people to improve our international competitiveness in the field of materials science. We are eager to discover novel materials and develop practical materials that will change the world and to determine the ways to contribute in strategic areas such as carbon neutrality, quantum materials, and wellbeing, and I will steer NIMS to promote fundamental research that will contribute to Japan's industrial competitiveness.

Your continued understanding and support will be greatly appreciated.

Kazuhito Hashimoto

Former president, National Institute for Materials Science (NIMS)

Effective March 31, 2022, I have resigned from my position as President of NIMS after serving for six years and three months. Although I had one year left in my contract, I decided to resign at this time in the belief that the next medium-to-long-term (MTLT) plan starting in FY2023 should be implemented under the direction of a new president. I greatly appreciate the support I have received from NIMS and others during my tenure.

The mission of a national research and development agency is to contribute to society by achieving significant research results. To this end, I encouraged NIMS researchers to enhance their research capabilities both at the individual and team levels. They have responded positively to my expectations and produced tangible results.

For example, the number of research papers published—a research capability indicator—has increased from 1,222 in FY2015, immediately before the implementation of the current MTLT plan, to 1,564 in FY2021 as of March 31, 2022. In addition, in terms of the number of citations per paper—another research capability indicator—NIMS has substantially surpassed Japan's universities and other national research and development agencies and is now neck-and-neck with world-class research universities overseas, including the University of Cambridge, the California Institute of Technology and the Massachusetts Institute of Technology.

With respect to NIMS' organizational efforts, it has been selected as a central hub for several major national projects related to rechargeable batteries, liquid hydrogen, materials informatics and other technologies, building a reputation as a key player in Japanese materials research. In addition, we have been leveraging our team research capabilities in large-scale joint research with other organizations. In these research projects, we always keep our greater goal in mind: improving Japan's overall research capabilities. For example, we have made huge labor and financial investments in our efforts to develop materials data platforms with the goal of making them available to the entire academic sector. During this project, we negotiated with the Japanese government, driving MEXT (the Ministry of Education, Culture, Sports, Science and Technology) to launch a new project in FY2021 to develop advanced materials research infrastructure across Japan.

NIMS has also worked to help boost Japan's industrial competitiveness. For example, we have created Materials Open Platforms (MOPs): an industry-specific collaboration framework to encourage rival private companies to jointly conduct basic research to achieve common goals, with NIMS mediating their collaboration. MOPs are currently in operation for the chemical, all-solid-state battery, pharmaceutical and magnet industries. I believe that these efforts have been effective in strengthening the international competitiveness of Japanese industry because most domestic manufacturers are small relative to their counterparts overseas. I look forward to further developments in the MOP project.

Finally, the research environment at NIMS has significantly improved during the current MTLT plan period thanks to support from MEXT and the financial authorities. The quality of our research equipment is undoubtedly top notch among materials research organizations around the world. I hope that NIMS will leverage this advantage to make great advances in the future. We appreciate your continued support of NIMS, which is dedicated to working hard for the public.

THE ECCENTRIC VIEWS
OF MATERIALS SCIENTISTS

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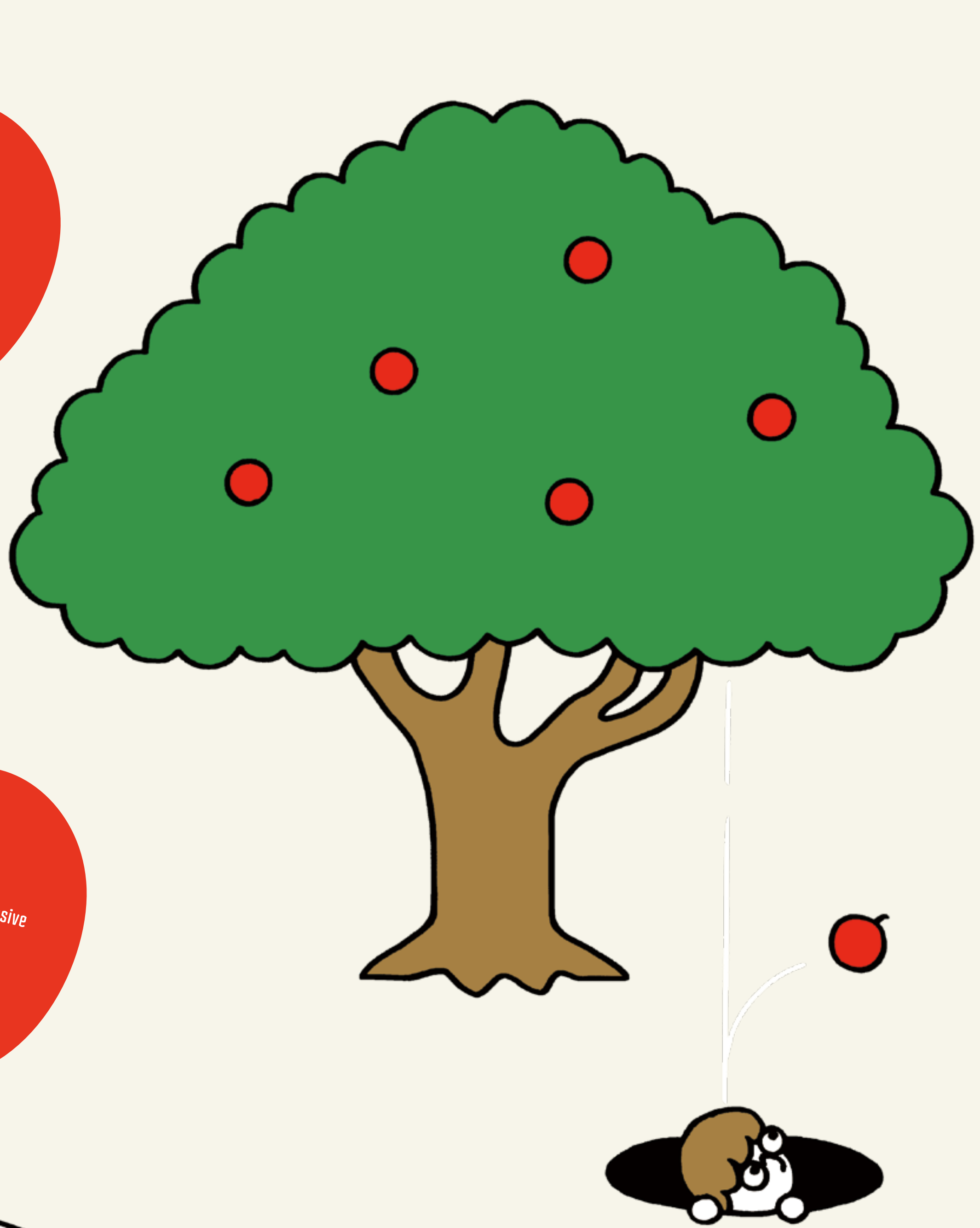
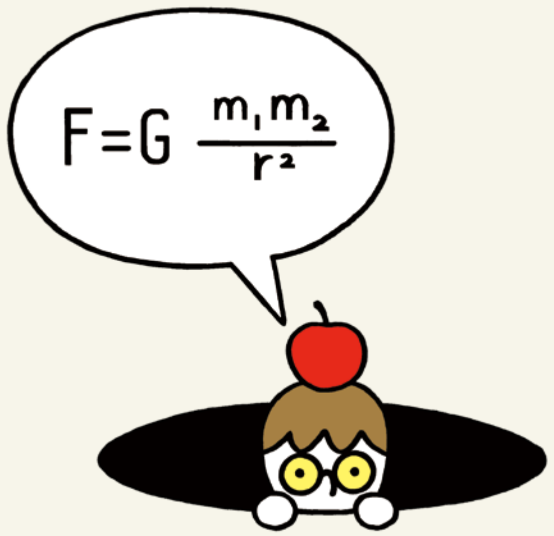


Seeing an apple fall from a tree would be a mundane event for most of us.
When Isaac Newton saw this,
he perceived a force of attraction acting between Earth and the apple.
This insight ultimately led him to formulate the law of universal gravitation.

Unconventional ways of thinking, viewpoints and approaches are important for scientists as they pursue new discoveries.
Some become captivated by phenomena that may appear trivial to most people and some may find inspiration even in failed experiments.
They are filled with a sense of curiosity and discovery and tirelessly seek answers through a multidisciplinary, varied research approach.

These research efforts sometimes bear fruit in the form of new discoveries and new materials. Materials scientists at NIMS have also discovered amazing new materials by taking an unconventional approach and using their keen insights into everyday phenomena.



非常識な『ミカタ』～材料の科学者はこう考えた～

Example 1

Revealing coconut crab claw microstructures: clue to the development of extremely tough materials

The eccentric views of materials scientists

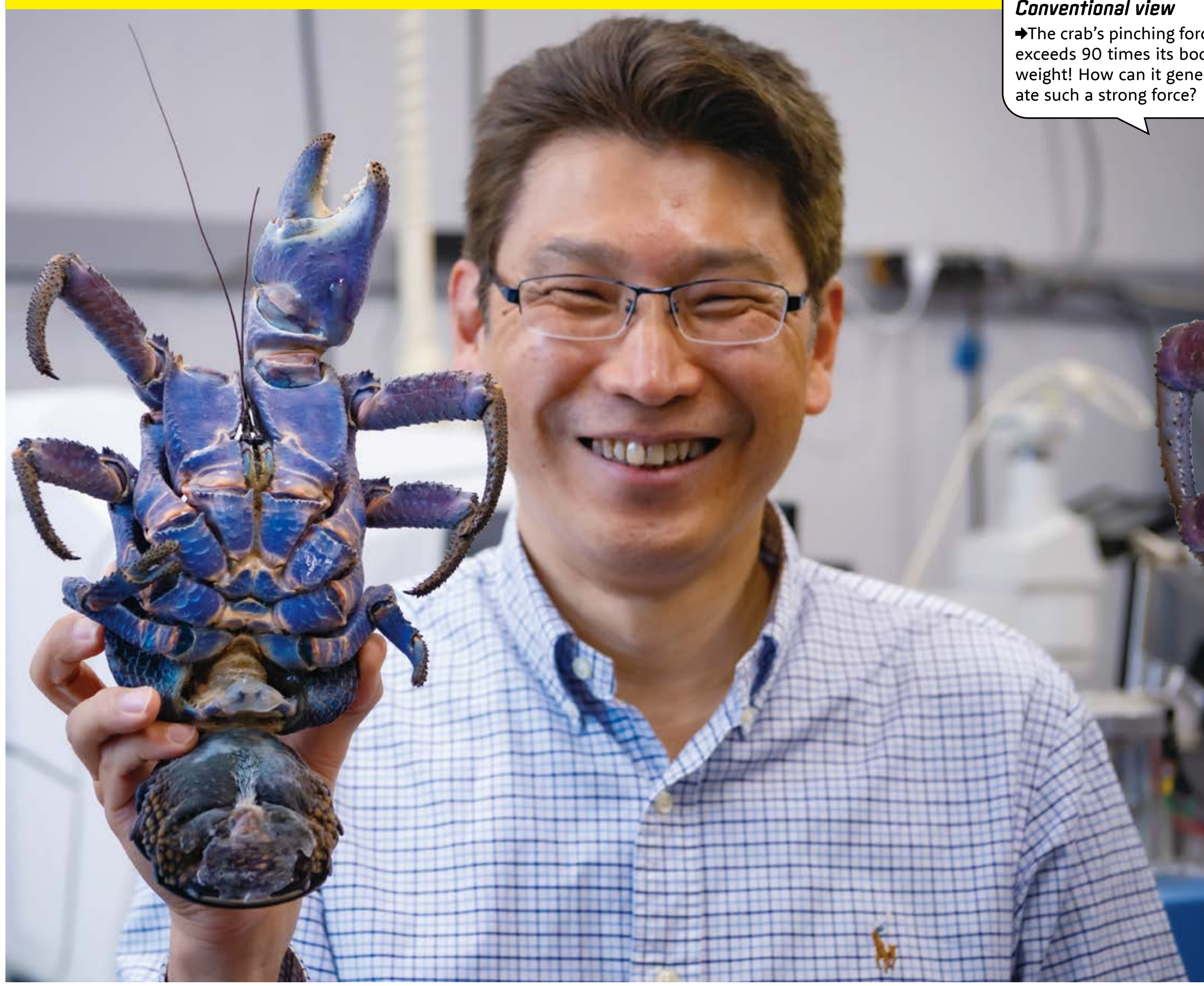
Dr. Tadanobu Inoue's view

➡How can the crab's claws withstand such an enormous pinching force without breaking?

The coconut crab is a rare hermit crab species inhabiting the areas around Okinawa in Japan. It is also one of the largest terrestrial crustaceans. Tadanobu Inoue has been researching strong, breakage-resistant steel for many years and previously succeeded in developing a very strong, tough steel material. When he was struggling to develop even stronger, tougher materials, he read about the coconut crab, which can deliver a pinching force 90 times its body weight—equivalent to a lion's bite. His first reaction was unique: instead of wondering how powerful the crab's claws are, he was impressed by the fact that they can withstand such great force without breaking. This remarkable ability inspired him to begin researching coconut crab claws. He eventually revealed their amazing microstructure and is now attempting to apply it to the development of extremely strong, tough materials.

Conventional view

➡The crab's pinching force exceeds 90 times its body weight! How can it generate such a strong force?



Coconut crab Inoue obtained in Okinawa. This frozen specimen is brightly colored.

My ambition early in my research career was to create stronger, tougher materials. This led me to focus mainly on steel materials research for many years. A material's susceptibility to breakage usually increases with increased strength. Contrary to this general tendency, I've been seeking to create materials that are both strong and ductile (i.e., durable).

In 2008, I succeeded in creating a strong, tough steel material with an optimum combination of strength and ductility and published an article about it in Science. This steel, which is resistant to fracture in a manner similar to bamboo, generated a huge, positive response. I also developed some products using this material. After these accomplishments, I continued my research with the desire to create even stronger, tougher materials.

Over the following decade, I was unable to find materials superior in quality to the steel material I had previously developed. I was about to give up this line of research and begin considering other research directions.

However, one day in 2018, I had a sudden epiphany that living creatures may provide insights that are helpful in creating strong, tough materials. I did an internet search using a combination of keywords: organisms, strongest, toughness and materials. One result grabbed my attention: a 2016 press release published by the Okinawa Churashima Foundation, which reported that the pinching force of the coconut crab was equivalent to the biting force of a lion.

I didn't know anything about coconut crabs at the time, but I was impressed to learn that its pinching force is 90 times its body weight. I wondered how it was possible for these claws to withstand such a huge force without breaking. I speculated that such powerful claws must have a very unique internal structure that I had never seen. I became very excited and immediately traveled to Okinawa.

I visited the Okinawa Churashima Foundation and shared my interest in studying the microstructure of coconut crab claws to understand why the claws are so resistant to breakage. The staff seemed surprised by my peculiar interest. Convinced by my enthusiasm, the staff provided me with coconut crab claws preserved in formalin.

After returning to NIMS, I immediately began studying the claws—the first biological research I had ever done. Without any knowledge or guidance, I took the approach that I was familiar with from studying metallic materials: I first polished the surfaces of the claws and measured their hardness. It was approximately 250 HV—equivalent to the hardness of high-strength steel. This was surprising given that the claws are composed mainly of calcium carbonate. The subsequent microscopic examination of the claw's exoskeleton revealed that it consisted of a hard outer layer and a soft inner layer. These preliminary results motivated me to engage in in-depth research.

In June 2019, I once again visited the Okinawa Churashima Foundation during the season in which coconut crabs are active. I observed the behavior of the crabs with the foundation staff at the Ocean Expo Park in the evening and purchased fresh coconut crabs at the market. The crabs are regarded as a delicacy and sell for relatively high prices. I told the crab sellers that these crabs I was purchasing would not be eaten and that I was studying their claws. They looked at me strangely. I froze the crabs and brought them back to NIMS with me.

I examined the claws' microstructure under a scanning electron microscope with the assistance of a scientist with expertise in biological tissues. Unfamiliar with biological systems, I was unable to fully understand what I was looking at. I subsequently broke a claw and microscopically observed the broken surface of the exoskeleton. The surface was not smooth and flat; instead, it appeared to be step/terrace fracture surface. When a strong force was applied to the exoskeleton, it was able to spread out the force over a larger area, making it resistant to fracture in a manner

Inoue prepared coconut crab specimens for in-depth research. His specimens have been stored in a display case with lighting.

Inoue observing the claw's exoskeletal layers under an optical microscope

similar to bamboo. In other words, fracture occurring in a small area of the exoskeleton does not extend to the surrounding areas, which was similar to what I had observed in the strong, tough steel I previously developed.

To examine the exoskeletal microstructure in even greater detail, I generated a three-dimensional image of it. This image revealed that the exoskeleton is composed of spiraling stacks of plates (made of chitin-protein fiber bundles) in an orderly arrangement with the stacks extending in a direction perpendicular to the exoskeletal surfaces (see "Outer layer" in the figure below). These spiral stacks are approximately 2.5 microns in thickness. Although lobsters have similar spiral structures in their exoskeletons, they are thicker (approximately 10 microns). Because metallic materials with finer microstructures are known to be harder, I spent decades seeking ways of making their microstructures finer. I discovered the solution (i.e., finer microstructures) in coconut crab claws.

The inner layer of the claw exoskeleton had a completely different microstructure from the outer layer. It was composed of soft tissues with numerous pores 100 to 300 nanometers (nm) in diameter extending in a direction perpendicular to the exoskeletal surfaces. These pores were arranged in an orderly fashion at an interval of 0.73 microns (see "Inner layer" in the figure below). I also found that nutrients and ions are transported through these pores. These soft tissues function as an energy-absorbing cushion to prevent the claws from collapsing. Another discovery was the existence of an intermediate layer with a distinctive structure that connects the hard outer tissue and the soft inner tissue.

After understanding the claw's exoskeletal morphology, I've moved on to the next stage in my research. Although we now know the hardness of the exoskeleton at a given point, I'd like to know the strength of a material with physical properties similar to those of the exoskeleton. For this purpose, I'm planning to develop a claw exoskeleton-inspired bulk material and examine its ductility. The result of this testing may help identify potential niches for this material.

Minimally invasive surgical techniques have been developed in medicine. One such technique involves the pinching of a diseased area within a narrow blood vessel using an endoscope with a pair of tiny forceps attached. I heard that a large pinching force is required to achieve this, and the physical properties of coconut crab claws may potentially be useful for this purpose. I will widely publicize this material to invite suggestions about its potentially beneficial and effective applications. Putting this material into practical use is my ultimate goal.

Cross-sections of coconut crab claw. It is a composite structure consisting of hard layers and soft layers.

Three-dimensional imaging of the claw's exoskeleton. First, an image of the claw surface is taken. The surface is then scraped to a depth of 15 nm using an ion beam and another image is taken at this depth. This process is repeated to take a series of images at different depths. Finally, these images are combined to generate a three-dimensional image.

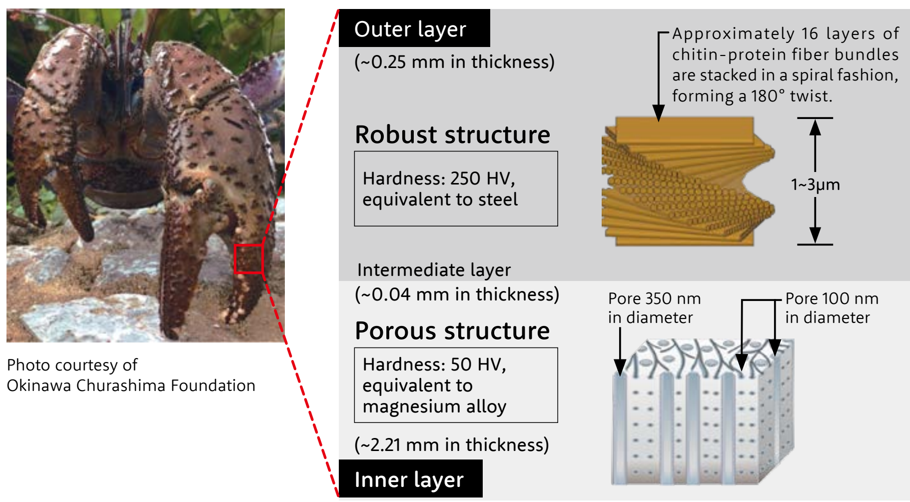


Photo courtesy of Okinawa Churashima Foundation

Tadanobu Inoue
Group Leader, Plasticity Processing Group
Field Director, Design and Producing Field
Research Center for Structural Materials

Example 2

Fine ceramic powder produced by accident: probing a mysterious phenomenon leads to the development of a new technique

The eccentric views of materials scientists

Dr. Naoki Ohashi's view

➡The experiment was clearly a failure, but an inexplicable phenomenon emerged as a result. Let's investigate its cause.

Conventional view
➡The experiment failed. Let's clean up the ruined samples.

Ceramics are normally hard, heat-resistant and chemically stable materials produced by sintering, i.e., firing shaped inorganic powders. However, Naoki Ohashi produced an unusually fine powder by firing ceramics. That was like a reverse process to sintering, and was happened due to an equipment malfunction. He was intrigued by this peculiar phenomenon and decided to investigate its mechanism. His research eventually revealed the reason why bulk ceramics were crushed by firing. He also succeeded in finding a way of regulating the grain size of the powder. This new technique, which Ohashi named chemothermal pulverization (CTP), could potentially be useful in recycling ceramics. In addition, CTP could potentially be used to produce functional inorganic materials for electronics, medical equipment, cosmetics etc.

Ohashi showing the electric furnace he uses to sinter ceramics. Sintering at high temperatures consistently produced hard ceramics, except on one occasion on which he found that the product had been reduced to a fluffy powder.

On the day of the experiment, the precursor was heated in a furnace filled with ammonia as before. The resultant products looked completely different from what we normally synthesized. They were supposed to be red-brown masses, but on this particular day, the obtained product was a fluffy, pure white powder (see the photo on p. 10). I had followed the same procedure: coarse white precursor powder turned into very fine white powder although heated in ammonia. Something had apparently gone wrong, leading to this totally unexpected result.

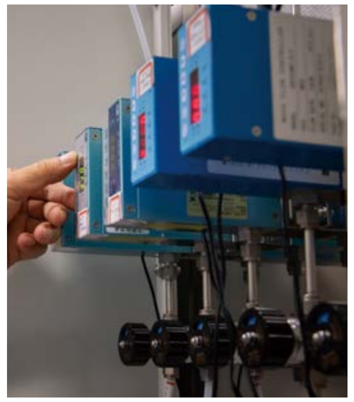
I eventually found that the gas piping was faulty and replacing it fixed the problem. Although I was glad that the problem had been identified, I was captivated by the mysterious fluffy powder. I subsequently began investigating how it had been produced alongside my other ongoing research projects.

Thorough study revealed that the strange outcome had been caused by the contamination of pure ammonia with a small amount of oxygen introduced through the faulty gas piping. Under simulated faulty piping conditions, heating the precursor once again produced a white fluffy powder. Although heating the precursor

Procedure for decomposing a raw ceramic material into a fine powder

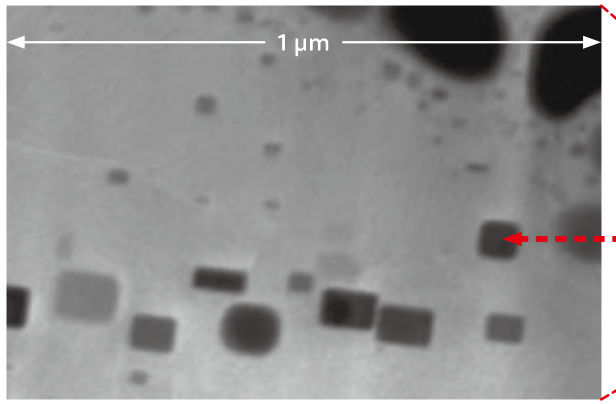
Place approximately 2 g of raw ceramic particles in a sample container.

Set the filled sample container in the electric furnace.

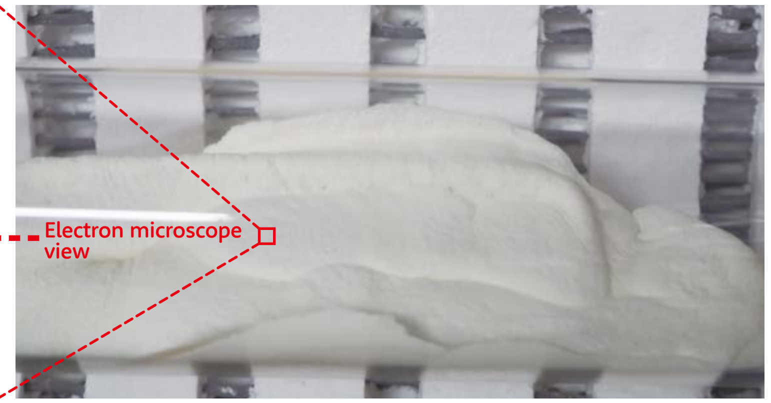


Adjust the concentrations of ammonia and oxygen.

Approximately 48 hours later

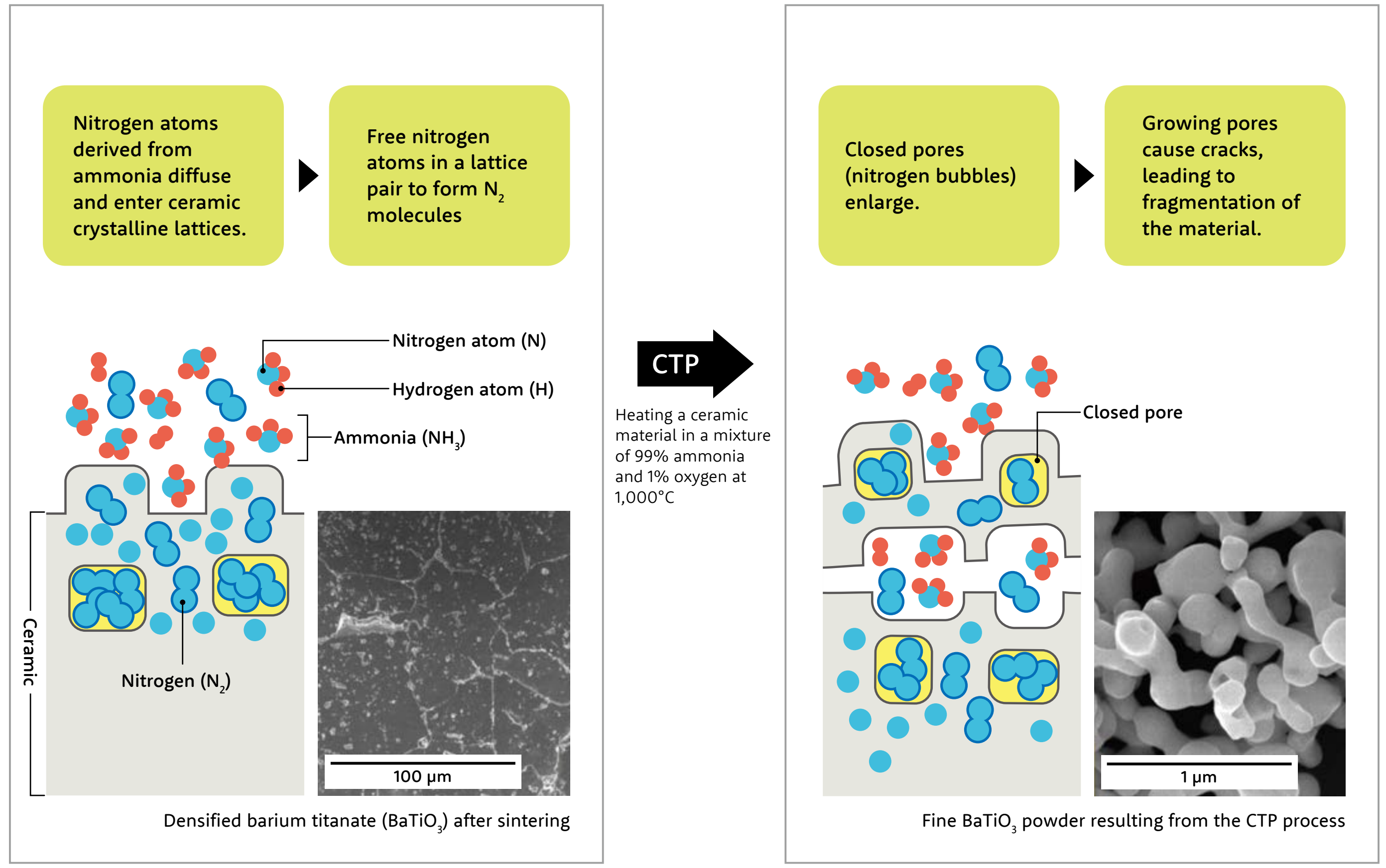


Numerous rectangular pores can be seen on the powder surface.



Fluffy, pure white powder resulting from chemothermal pulverization has spilled out of the container.

Chemothermal pulverization (CTP) of a raw ceramic material



N. Ohashi et al., "Chemothermal pulverization: Crushing titanate crystals to obtain nanosized powders via high-temperature treatment." Journal of the American Ceramic Society. 105 [3] (2022) 1913-1927.

powder normally induces agglomelation and densification, sintering was not induced under these specific conditions, i.e., ammonia stream containing oxygen. In addition, the precursor powder was found to transform into a fine, fluffy powder without exhibiting phase separation. This phenomenon was inexplicable to me even though I had been researching ceramics for many years. I formulated several hypotheses and spent many hours investigating them without success. Even so, I needed the words to present this strange phenomenon and I started to use the term, "Chemothermal pulverization (CTP)" as I assumed this phenomena was resulting from chemical activity of ammonia and thermal activation of reaction.

Sintering is a thermal process by which loosely packed particles are densified to be a hard ceramic, and it's an entirely predictable thermodynamic process. However, what we saw was somehow caused crystalline particles to disintegrate into a finer powder. Because this was the first time I had encountered this phenomenon, I tried to report this phenomenon by submitting a manuscript to a scientific journal. After a while, publication was rejected because the process leading to the phenomenon was not sufficiently explained, although the reviewers found it interesting.

I eventually worked out the mechanism by which heated crystalline ceramic particles disintegrate. First, nitride ions derived from the decomposition of ammonia enter into a crystal. As free nitride ions move around within the crystal, they bump into each other and pair to form nitrogen (N_2) molecules. These molecules are very stable and resistant to being split even at a temperature of 1,000°C. As the number of nitrogen molecules within a crystal increases, they start creating pores in which they are trapped. As these pores enlarge, the crystal cracks and breaks into finer pieces. The oxygen introduced due to the equipment malfunction prevents the oxides from decomposition and nitridation, facilitating the disintegration of the crystalline ceramic particles (see the figure on p. 11).

I've since gained a better understanding of the ways in which nitrogen molecules and pores form. With this insight, I'm developing a technique that enables controlling of grain size of the powder. To this end, it is really necessary to manage complicated chemical process at high temperature. I now confirm that what we develop is actually "Chemothermal pulverization (CTP)".

Because CTP could possibly be used to break down hard, stable ceramic products into original, raw ceramic particles, I initially thought that it could be used in recycling.

For example, the CTP technique could be used to recycle the ceramics heaters. While old-fashioned electric heaters have exposed heating elements which turn red when hot, modern heater have their heating elements concealed in a flat ceramic plates. Because the coils are embedded within the ceramics, extracting the metal coils from ceramic plate is difficult. To address this issue, the CTP technique could be used to disintegrate the outer ceramic component, allowing easy recycling of the metals embedded in the ceramic devices.

After I publicized information on the CTP technique, which is capable of disintegrating ceramic particles, I received many responses, including some unrelated to recycling. It's very important and challenging for them to adjust the sizes of powder grains while maintaining their purity.

Traditionally, fine clay powder used as a source material for potteries and porcelains has been produced by mechanical processes, e.g., grinding and sieving. When source materials are mechanically crushed, the equipment wears down: consequently, source materials must be contaminated. This makes it difficult to prepare fine ceramic source powder without reducing their purity. The CTP technique may be used to achieve this as it is able to break down grains without introducing impurities.

The technique may also be used to disperse aggregates and agglomerates into a fluffy powder with uniform grain size, thereby significantly improving their ease of use and value. This is somewhat similar to preparing cake batter without lumps to improve the quality of the baked product.

This particular failed experiment produced a very peculiar phenomenon. I found it very captivating and my investigation into its cause led to new discoveries. Discussion with my colleagues also helped me solve mysteries and identify potential applications for the CTP technique. My horizons as a researcher are broadening through this project. I look forward to seeing further developments.

Naoki Ohashi
Group Leader, Electroceramics Group
Field Director,Electric and Electronic Materials Field
Director, Research Center for Functional Materials

Example 3

Strong yet easily removable adhesive inspired by the wall-climbing footpads of flies

The eccentric views of materials scientists

Dr. Naoe Hosoda's view
➡Flies' footpads are capable of alternately attaching to and detaching from a walking surface.

Conventional view
➡A fly crawling around on the wall... gross!

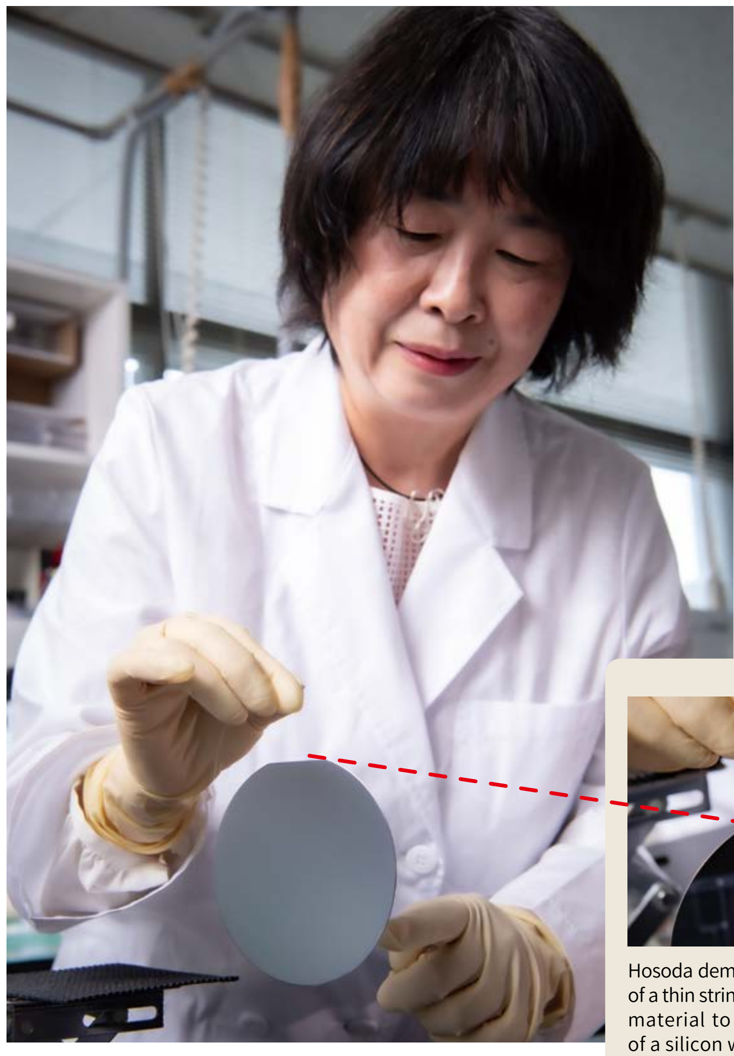
Products whose parts are firmly glued together are difficult to disassemble and recycle at the end of their service lives. Addressing this issue requires the development of strong yet easily removable adhesives. A research group led by Naoe Hosoda has developed a fly-inspired adhesive material with these characteristics. Hosoda initially saw flies climbing walls and interpreted this as an ability by flies to alternately attach their feet to and detach them from the wall surface. After closely studying the way in which flies' footpads are formed during their metamorphosis, her group succeeded in developing a next-generation adhesive by mimicking the structure and mechanism of fly footpads.

Making products more recyclable is important in promoting a circular economy. Existing joining and bonding technologies are designed to permanently bind materials together. Separating materials glued together in this way requires huge amounts of energy, rendering many waste products unrecyclable and leading to their disposal without disassembly. One of my research objectives as an adhesive materials developer is to create strong yet easily removable adhesives.

It's very challenging to develop adhesives with both high bonding strength and the ability to be easily removed. I have been tackling this challenge through various strategies and approaches.

Insects are capable of climbing up vertical walls without falling off by alternately attaching their feet to and detaching them from the wall. I found this ability very interesting and began considering ways of applying it to the development of new technologies.

In addition to insects, I previously focused on plants as a source of inspiration for my research. I used to wonder why many plants shed their leaves in the fall and came to the conclusion that they're capable of doing so at an optimum time by design. This was a new insight for me and I actually developed and patented an adhesive material into which I incorporated the leaf-shedding mechanism of plants.



Check!

Hosoda demonstrating the ability of a thin string of the new adhesive material to support the weight of a silicon wafer.

Biomimetics is a longstanding approach to developing new technologies by mimicking biological structures and functions. This field of science contrasts sharply with rapidly advancing nanotechnology, which has enabled precise structural manipulation at the nanoscale. Nanotechnology has some disadvantages, however. Fabricating products using cutting-edge nanotechnologies and nano-processing is enormously expensive, hindering their practical and widespread use. Moreover, nano-processing requires a vast amount of energy and is counterproductive to efforts to promote a circular economy.

By contrast, living organisms are able to produce elaborate structures using widely available materials at ambient temperatures. I've been seeking ways of creating new materials in a manner similar to organisms.

To develop new adhesive materials, I focused on flies as a model. A fly's footpad (tarsus) has spatula-shaped hairs (setae) that enable a fly to walk on the wall as they alternately attach to and detach from the walking surface. I studied the way in which flies develop spatulate tarsal setae as they undergo metamorphosis during their pupal stage. Unlike human hair, which grows outward from its base, these setae were found to grow inward from their tips. In-depth research with Hokkaido University of Education and others has revealed that the seta's distal tip is composed of an elongated seta-forming cell and cytoskeletal actin filaments that form a framework. This tip structure solidifies into a spatula shape by reacting with the secreted cuticle.

We developed a fly-inspired adhesive material through a simple process similar to the way in which spatulate setae are formed in flies. First, a pair of nylon fibers approximately 50 microns in diameter are dipped into a sodium alginate solution. They are then pulled out of the solution, causing them to join into a single string with a spatula-shaped tip. Finally, this product is allowed to solidify (see the figure below). This process can be achieved at ambient temperatures without special equipment.

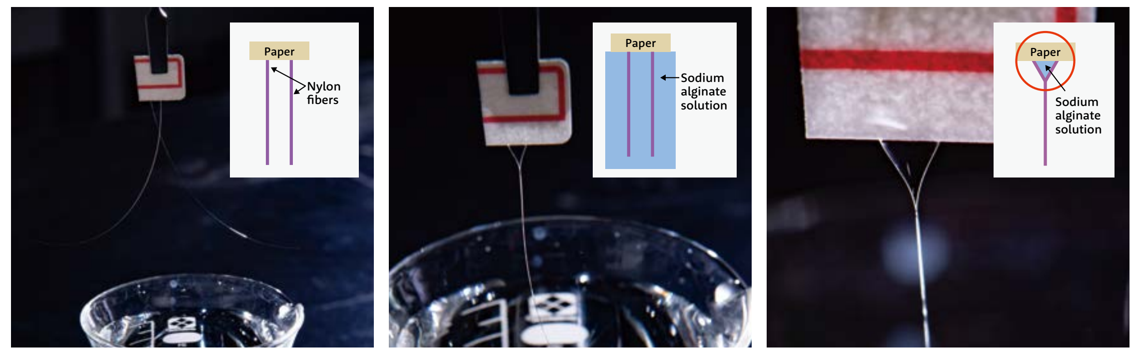
A string of this adhesive material is able to support the weight of an eight-inch silicon wafer and a bundle of 756 strings is estimated to be able to support a person weighing 60 kg. In addition, this material is easily removable.

The strength of the attachment between an insect's tarsi and the walking surface differs depending on the direction in which the strength is measured.* We were able to incorporate this adhesion mechanism into our fly-inspired adhesive material. This directional adhesiveness may potentially be applicable to technologies designed to grab and release objects, including robotic arms.

In addition to the projects mentioned above, we have started researching adhesive materials inspired by other organisms. I believe that insects and other creatures found in nature could potentially be able to provide us with more inspirations leading to great new technologies. Living organisms are truly amazing and fascinating research subjects.

* When an insect is walking on the wall, the adhesive strength of its tarsi is high in the direction parallel to the wall surface and low in the direction perpendicular to it.

Steps for preparing the strong yet easily detachable adhesive material inspired by flies' tarsal structure



A pair of nylon fibers (approximately 50 μm in diameter) will form a framework for the adhesive material.

Dip the fibers into a sodium alginate solution.

Remove the fibers from the solution, which causes them to join into a single string with a spatula-shaped tip.

Living creatures found in nature are a rich source of inspiration leading to new technologies!

Electron microscope image of a fly's footpad with spatula-shaped adhesive setae.

Naoe Hosoda
Group Leader, Surface and Adhesion Science Group
Bonding and Manufacturing Field
Research Center for Structural Materials

Example 4

Overcoming a disadvantage of silicon leads to a breakthrough in the development of next-generation batteries

The eccentric views of materials scientists

Dr. Narumi Ohta's view

➜Silicon's propensity to swell, which had been considered a disadvantage, can be exploited as an advantage.

Conventional view
➜Silicon's swelling makes it impractical. Let's try something else.

Conventional lithium-ion rechargeable batteries generate electric current by allowing lithium ions to travel back and forth between their electrodes through a liquid electrolyte. All-solid-state batteries (ASSBs) contain solid electrolytes instead of liquid ones and are expected to be safer and compatible with further miniaturization. ASSBs have already achieved energy densities equivalent to those of lithium-ion batteries. To further increase the capacity of ASSBs, research is underway to develop batteries equipped with a silicon anode capable of absorbing and storing a large amount of lithium ions. However, the silicon anode has a serious drawback: as its silicon component absorbs lithium ions, it expands dramatically, while its non-silicon component resists absorbing ions and maintains its volume. This differential expansion causes cracks to form between the two components, leading to structural failure. Despite this drawback exhibited by silicon anodes, Narumi Ohta was able to advance ASSB research and development by actually taking advantage of silicon's swelling.

For ASSBs to surpass currently available lithium-ion batteries in performance, they will need to be able to generate larger electric currents and store larger amounts of electricity. Graphite is the most commonly used anode material in lithium-ion batteries. However, silicon alloys are known to be able to store larger amounts of electricity than graphite due to their ability to absorb larger amounts of lithium ions.

Silicon anodes haven't been put into practical use because they expand dramatically as they absorb large amounts of lithium ions. While the volume of a graphite anode increases by only 12% as it absorbs lithium ions, the volume of a silicon anode balloons 300%.

The silicon particles used in ASSB anodes need to be mixed with solid electrolyte particles in order to create passages through which lithium ions can pass. This composition causes a major problem: when the anode absorbs lithium ions, the silicon particles expand while the solid electrolyte particles don't, causing cracks to form between them and leading to anode failure.

When I observed a charged silicon anode using an electron microscope, I noticed that the gaps between the silicon particles were completely filled in areas in which they aggregated. In other words, as the silicon particles expanded by absorbing lithium ions, they transformed into a continuous film.

In another ongoing project, I synthesized silicon films using a vapor deposition method*, integrated them into ASSBs and tested their performance. This project revealed that ASSBs equipped with relatively thick, continuous silicon films (1-3 µm in thickness) exhibit stable cycles and can generate large amounts of power. As described above, individual silicon particles were found to transform into a continuous film as they absorb lithium ions and expand. I realized that this simple phenomenon could be used to form continuous silicon films instead of the more laborious vapor deposition method, which requires a vacuum and high voltage. I also became aware of the fact that this phenomenon could be used to create silicon anodes composed exclusively of silicon particles without solid electrolyte particles.

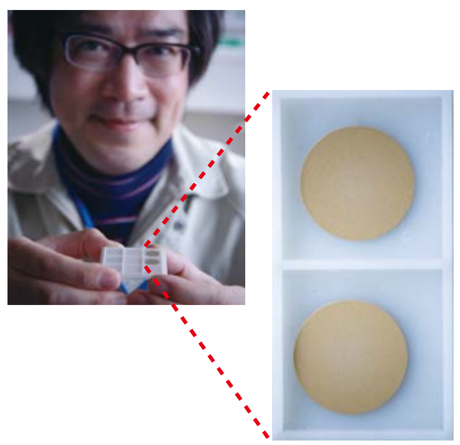
Previous research had found that silicon is an unsuitable electrode material due to its susceptibility to excessive expansion, which leads to anode failure, even though it is capable of absorbing a large amount of lithium ions. However, I discovered that silicon also can be used very effectively and advantageously.

After my discovery, I attempted to form a stack of uniform silicon particle layers on the surface of a current collector. However, I was unable to uniformly layer silicon particles using conventional micro-sized particles. I then tried smaller nanoparticles for this procedure.

I also tested various particle application methods and found that spray depositing silicon particles layer by layer on the surface of a stainless-steel substrate was most effective. Using this method, I was able to form a uniform stack of 10 layers. I then integrated this into an ASSB and charged it. As a result, the layered silicon particles expanded and formed what appeared to be a continuous film.

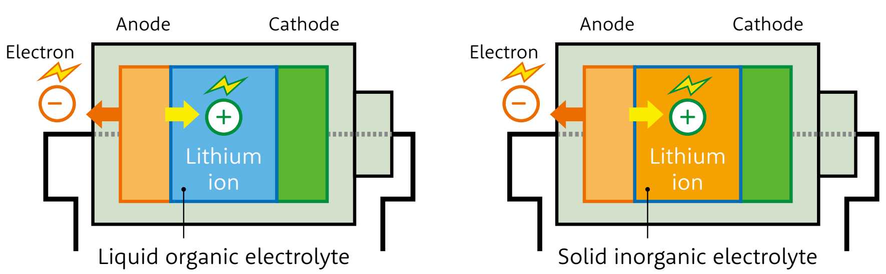
By leveraging the swelling property of silicon, I found a simple way of forming a continuous film using silicon nanoparticles. This is a major step forward in achieving practical use of ASSBs.

Although I had been researching ASSBs equipped with a sulfide electrolyte, sulfides are known to be reactive with moisture and therefore need to be protected from exposure to the air. Because of this disadvantage associated with sulfide ASSBs, NIMS is now fully focused on the development of oxide ASSBs. Oxides are stable in the air and highly compatible with existing production lines. Sulfide ASSBs are expected to be put into commercial use in the near future. In my current research, I'm comparing oxide ASSBs with sulfide ones to identify similar capabilities and issues needing to be addressed.



Silicon films Ohta has synthesized (Approximately 1cm in diameter). They can be used as anodes for all-solid-state batteries without further processing.

A lithium-ion battery and an all-solid-state battery



*Vapor deposition is a film synthesis method in which a gaseous raw material is deposited onto a substrate surface in a vacuum chamber to form films. This method is applicable to many different materials.

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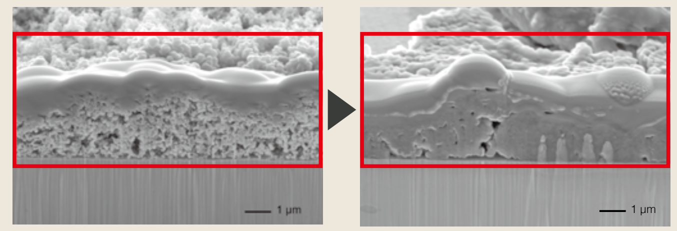


Before charging / After charging

Cross-sections of an electrode composed of silicon nanoparticles before and after charging. Charged, swollen particles collectively formed a continuous film.

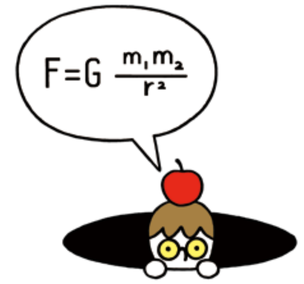
Preparing anodes composed exclusively of silicon particles

1 Silicon nanoparticles are suspended in ethanol.

2 The suspension is then placed into a sprayer.

3 A thin layer of silicon is sprayed onto circular stainless-steel substrates.

4 The spraying is repeated 10 times to uniformly distribute nanoparticles across the substrates.



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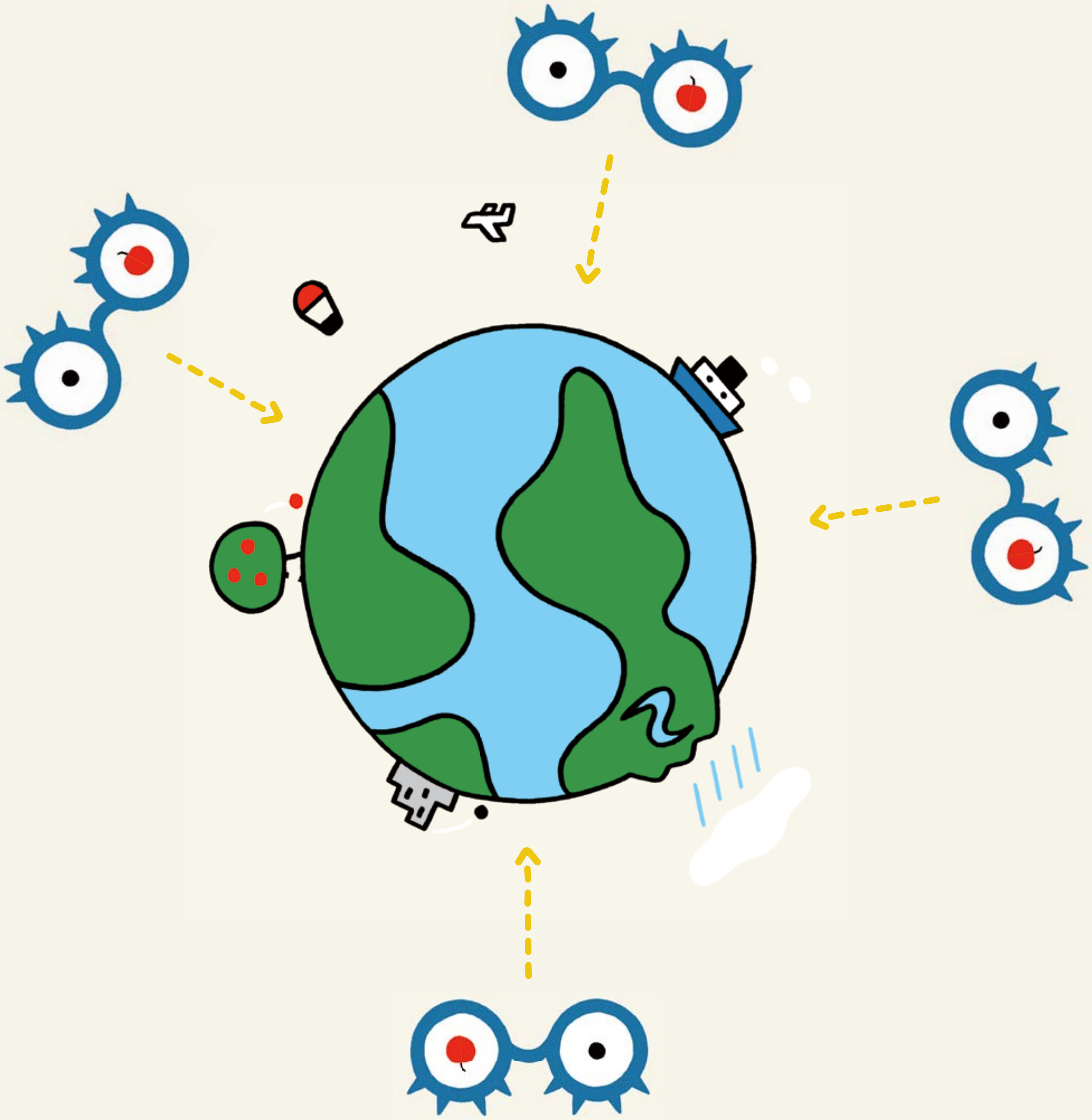
The eccentric views of materials scientists



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