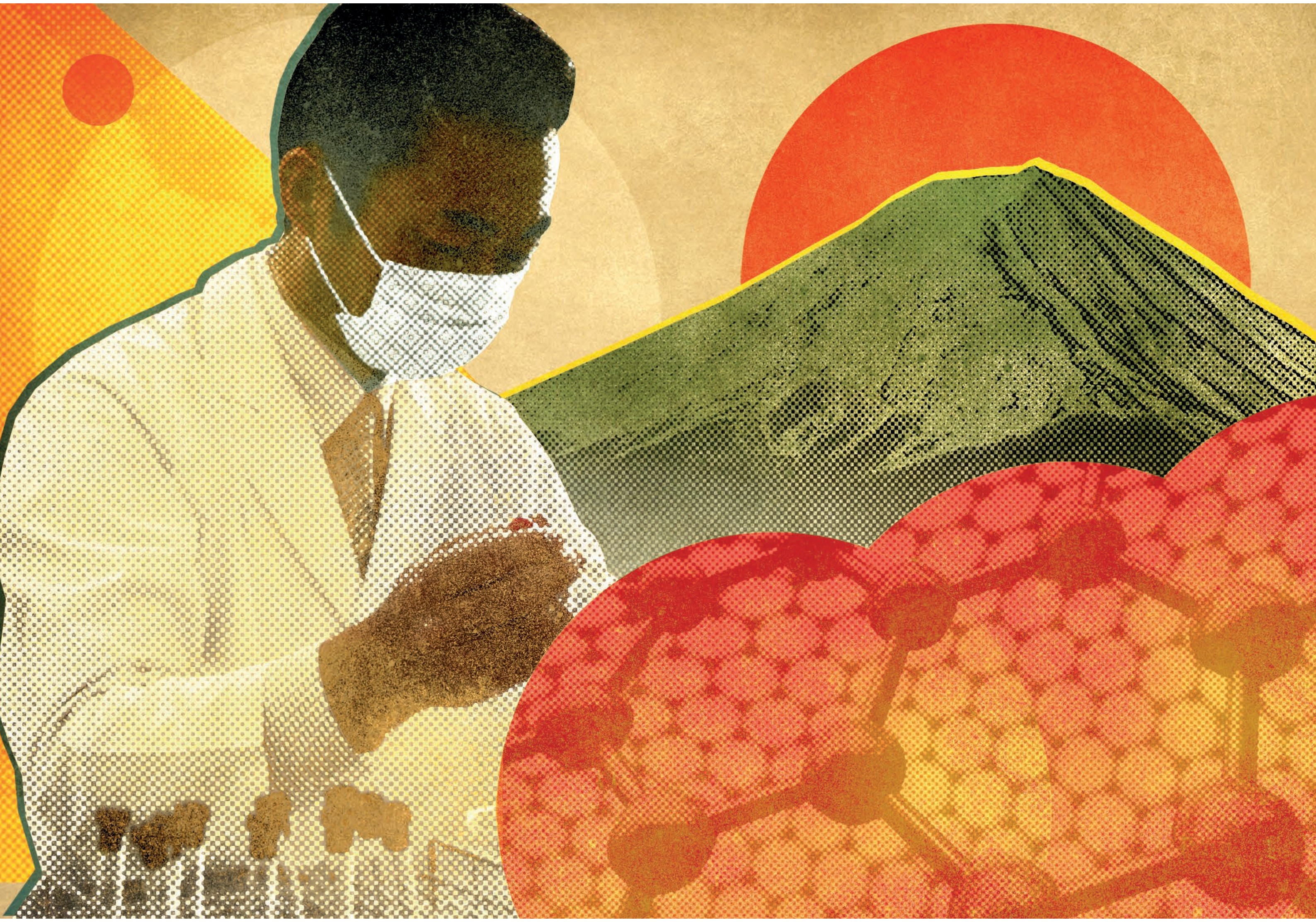


ILLUSTRATION BY PETER HORVATH; PHOTOS: GETTY

Catching up with carbon

Japan fights to stay on top of a field it pioneered.

BY TIM HORNYAK

In September last year, a handful of researchers were sitting around a computer monitor in chemist Kenchiro Itami's lab at Japan's Nagoya University as one loaded a file showing the results of an X-ray crystallography scan. Within seconds, the room erupted: scientists were on their feet, cheering and exchanging high fives. In front of them was a 3D representation of a carbon nanobelt — a new molecule of carbon that the team had successfully synthesized after 12 years of painstaking effort.

"Without these data, we couldn't prove its structure 100%," says Itami, director of the Institute of Transformative Bio-Molecules at Nagoya University. "It was the most exciting moment I ever had in my life."

Itami thinks he has good reason to be so excited. "The discovery of a new form of carbon has always opened up new science and technology — fullerenes are a great example," he says, referring to the all-carbon molecular spheres created by scientists at Rice University in Houston, Texas, in 1985.

Chemists have indeed tried many things when it comes to constructing exotic forms, or allotropes, of carbon: nanobelts are only the latest and it's significant that a Japanese team made them. The country has enjoyed a rich history of manipulating carbon — an atom with the stability and strength to build complex molecules — into new materials with useful properties, and it has built a strong industrial sector from those basic research efforts.

But in the past decade or so, Japan has found itself beset by international competition, as progress in the field has shifted abroad. Now, Japanese researchers are fighting to maintain their global prominence.

NO SMALL PEDIGREE

The history of nanocarbons is nearly as intricate as the structures themselves. Smiths have forged carbon with metal to make sharp, resilient weapons for thousands of years, with ▶

some astonishing results: a 2006 analysis of Damascus sabre steel from the seventeenth century[1] revealed that the material contains microstructures such as carbon nanotubes — lattices of carbon atoms arranged to create a pipe with a diameter of 0.7–50 nanometres.

Modern synthesis of carbon nanotubes is widely attributed to Japanese scientists Morinobu Endo and Sumio Iijima. When Endo was working at the French National Centre for Scientific Research (CNRS) in the 1970s, he synthesized carbon fibres that featured hollow tubes arranged in concentric sheets like the rings of a tree. Sixteen years later, Iijima published a letter in *Nature* entitled 'Helical microtubules of graphitic carbon'; he is often cited as the scientist who discovered carbon nanotubes[2].

But who first made the discovery is still a topic of discussion. A 2006 editorial in *Carbon*[3] suggested that Russian scientists L. V. Radushkevich and V. M. Lukyanovich should be credited for their 1952 paper[4], which reported that "carbon filaments could be hollow and have a nanometre-size diameter". The paper, published in Russian, was little-known outside the Soviet Union, and it was Japanese researchers who were responsible for opening up the field to the rest of the world. "From the beginning of the discovery, I was confident in the importance of nanotubes," says Iijima, now a chemist at Meijo University in Nagoya.

He turned out to be right. The strength-to-weight ratio of the tiny molecules is at least 30 times greater than for Kevlar, the material used in bulletproof vests. Adding nanotube fibres to just about any material — from vehicle parts to golf-club shafts to elevator cables — will strengthen it enormously. And because they can conduct electricity better than copper, nanotubes have given rise to products such as transparent conductive films and even prototype computers.

As with many new materials, some applications can be unexpected. For instance, a nanotube yarn originally designed for lightweight data cables was re-engineered for use in space. NASA scientists think that the yarn — 200 times stronger and 5 times more elastic than steel — could significantly lower the overall mass of a spacecraft.

Itami's carbon nanobelt is, essentially, the single repeating unit of a relatively tiny carbon nanotube (see 'Nanocarbon molecules: a glossary'). But the simplicity of the nanobelt is misleading — synthesizing one is supremely difficult owing to the high degree of strain placed on the 12 benzene rings that must be joined together to create the belt.

EXCELLENT CHEMISTS AND PHYSICISTS ARE STILL IN JAPAN BUT THE TREND FOR TRAINING YOUNG JAPANESE SCIENTISTS IS DECREASING.

The effort could well be worthwhile, however. Nanobelts have been described as 'dream molecules' by researchers, because of their potential roles in everything from semiconductors to photonics equipment. They might even serve as "seeds" for growing "structurally well-defined carbon nanotubes", Itami and his colleagues reported this year[5].

Itami hopes that carbon nanobelts will become available to businesses in a matter of months. If they do, they will be making their way into a commercial field that is steadily filling up with exotic forms of carbon. A material known as Vantablack comprises millions of vertically aligned nanotubes, each with a diameter of about 20 nanometres. The nanotubes absorb 99.96% of incident radiation, according to Vantablack's developers, Surrey NanoSystems in Newhaven, UK. That makes Vantablack the darkest synthetic substance in the world. As such, it could be used to protect telescopes from stray light, making it easier to see faint stars, or to improve the optical performance of satellites, among other applications.

And in 2013, researchers at Stanford University in California reported[6] that they had made a basic computer from carbon-nanotube transistors and simple electronic circuits. The device drew attention as a possible replacement for silicon and as a way to facilitate the development of ever-smaller transistors.

BARRIERS TO ENTRY

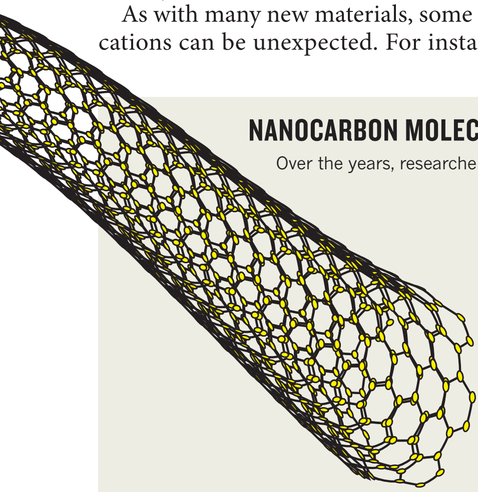
The promise of nanotubes has been somewhat overshadowed by their potential health dangers. The Japanese government has been evaluating nanotubes for possible carcinogenic effects, and some scientists have likened the tubes to asbestos in terms of health risk, In 2015, one joint French–US study[7] found nanotubes similar to those used in vehicle exhaust systems in tissue samples taken from 69 children in Paris with asthma. "These results strongly suggest that humans are routinely exposed to nanotubes," the authors wrote.

Another roadblock to the application of nanotubes is price — 1 gram can cost as much as US$250, around 6 times the price of gold. Mass production would bring down that cost considerably, so an important area in nanotube research is the development of alternatives to the expensive, high-energy methods currently used, such as arc electrical discharge and chemical vapour deposition.

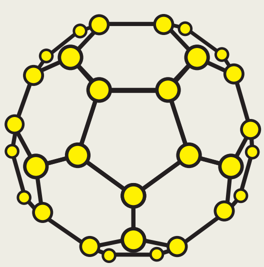
The possible effects on human health and the high price tag may have dampened global enthusiasm for nanocarbon products, and could have slowed down Japan's academic

NANOCARBON MOLECULES: A GLOSSARY

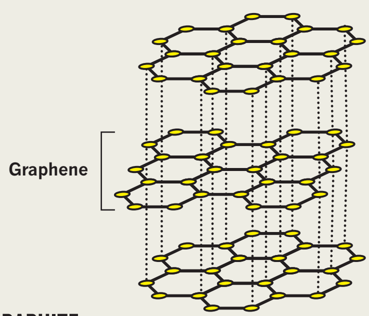
Over the years, researchers have built a dizzying collection of exotic forms of carbon.



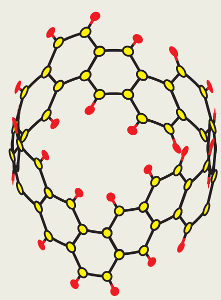
NANOTUBE
A sheet of hexagonally arranged carbon atoms, stretched to make a pipe shape. First formally described by scientists in 1952.



FULLERENE
A hollow sphere of carbon resembling a football. Synthesized in 1985.



GRAPHITE
Layers of hexagonally arranged carbon stacked on top of one another. Graphene — a single layer of this lattice — was isolated in 2004.



NANOBELT
The single repeating unit of a tiny carbon nanotube. Synthesized in 2016.

output. The country also faces challenges in terms of its academic workforce. "Excellent chemists and physicists are still in Japan but the trend for training young Japanese scientists is decreasing because students are not motivated to pursue PhDs any more — instead they want to finish a master's, as companies do not value PhDs," says Mauricio Terrones, a nanotechnologist at Pennsylvania State University in University Park and an editor at *Carbon*. "Therefore, Japan needs a new policy to motivate industry to hire PhDs from Japanese universities. In this way, the next generation of chemists and physicists will continue to be first-class and competitive worldwide."

Japan's research performance doesn't reflect the nuances of its relative strengths in the field. Japanese researchers excel in some areas, such as developing chemical techniques to grow nanotubes, but underperform in others, such as thermal engineering, says Takashi Kodama, a thermophysicist at the University of Tokyo.

Kodama returned to Japan early last year, after ten years at Stanford. "I've experienced both environments, the United States and Japan, and Japan's advantage is its high-tech equipment," he says. "Researchers here have easy access to excellent equipment at low cost, compared to the old, expensive equipment in the United States. Part of the reason is that it's easier to spend research funds in Japan on equipment instead of just human resources."

ECONOMIES OF SCALE

Although its academic output may be smaller than that of other science superpowers, Japan has continued to make significant contributions to the development and applications of nanotubes and carbon fibres, with state-backed research centres working closely with private companies to produce high-tech commercial products. Toray Industries in Tokyo announced in 2014 that it would be the sole supplier of carbon fibres for Boeing's upcoming 777X jet, extending its existing supply contract for the 787 Dreamliner, which made aviation history for its composite fuselage of carbon fibre coated with epoxy resin. Fujitsu, based in Tokyo and known for its supercomputers and servers, is looking into how nanotubes and graphene, another nanomaterial that has attracted immense interest, could help to miniaturize electronics.

Meanwhile, research organizations are continuing to expand understanding of the basic science of nanotubes while working on practical applications. Earlier this year, for example, the Tsukuba-based CNT-Application Research Center reported that it had developed a flexible, wearable nanotube strip that can sense and capture the hand movements of humans and robots. As a gesture-tracking device, it has potential health-care, information-technology and military applications.

In 2005, Yoshinori Ando, a materials scientist at Meijo University, set up Meijo Nano Carbon to manufacture nanotubes. In 2013, collaboration between Meijo Nano Carbon and Japan's National Institute of Advanced Industrial Science and Technology (AIST) led to a joint production plant that uses a technology known as enhanced direct injection pyrolytic synthesis. According to AIST, manufacturing speeds are 100 times greater than those achieved previously, with higher-quality end products. The company's hope is that mass production of high-quality nanotubes for the research and development market will accelerate commercial applications.

They face competition. In 2015, ZEON in Toyko began what it says was the first mass production of nanotubes using another technique developed at AIST, termed Super-growth. It expects to supply manufacturers of conductive and rubber materials and high-performance capacitors. Meanwhile, AIST is working with companies such as electronics maker Furukawa Electric in Tokyo, which is looking into how nanotubes could help to reduce the size of vehicle engines and therefore reduce carbon dioxide emissions.

Iijima is encouraged by the wide range of applications being explored. "Anyone can make a profit based on nanotube research in Japan or other countries," he says. And he isn't alone in his enthusiasm for Japan's market potential. "I believe Japan is still leading carbon science and technology — just look around and the major applications of carbon materials are being developed there," says Terrones. The fruits of this labour can be seen in the Boeing jets, sporting goods and oil-exploration equipment, he says. But he notes that companies are less willing than academic organizations to publicize their progress owing to intellectual-property concerns in a competitive sector.

As for Itami, the next step is to grow a nanobelt into a structurally pure nanotube. He also hopes to use nanobelts for small-molecule components in optoelectronic devices such as organic light-emitting diodes and solar cells.

"As in the history of fullerenes, one cannot really predict the extraordinary properties and functions of a new form of carbon," Itami says. "Perhaps trying to discover them is going to be one of the most exciting journeys for scientists." ■

Tim Hornyak *is a freelance science and technology journalist based in Tokyo.*

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The company driving the carbon electronics revolution

NEC IS LEADING the development of carbon nanostructures for a new breed of electronics.

Smaller transistors tend to be faster. It's a fact that has led the electronics industry to master the art of shrinking silicon transistors, doubling computing power every two years for the last half-century. Industry experts however predict that scaling will cease within four to seven years.

EVERY RESEARCHER AT NEC AIMS TO BECOME A PIONEER OF NEW TECHNOLOGY. IT'S A PART OF OUR CULTURE.

Just as silicon scaling has stalled, the variety of electronic devices being developed has exploded — and computation speed is often not a primary concern. For example, devices that make up the 'Internet of Things' (IoT) perform tasks like sensing, actuation and communication, rather than raw computation. Leveraging these IoT devices will require new energy-producing/storage devices with high efficiency, density and reliability.

These changes have focused attention on electronic materials beyond silicon, especially carbon. Like silicon, carbon has four valence electrons, and the two elements share some chemical and electrical properties. Unlike silicon, carbon can be easily made to form a variety of nanostructures with exceptional electronic and mechanical properties.

A great deal of work is still needed to make carbon nanostructures a viable material with useful electronic properties. As progress towards this goal gains pace, NEC has established itself as a research and thought leader in the field.

Tiny structures bring big opportunities

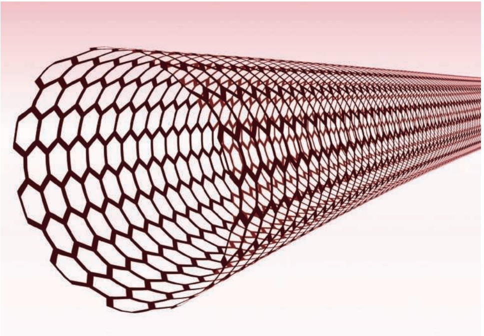
The discovery of carbon nanostructures coincided roughly with the development of the tools that enabled scientists to see them. Dr Sumio Iijima (above), a senior research fellow at NEC and former chief researcher of NEC's Fundamental Research Laboratories, was involved in both.

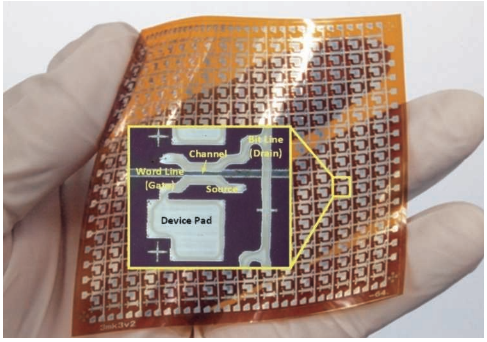
NEC researcher Dr Sumio Iijima first discovered carbon nanotubes in 1991.

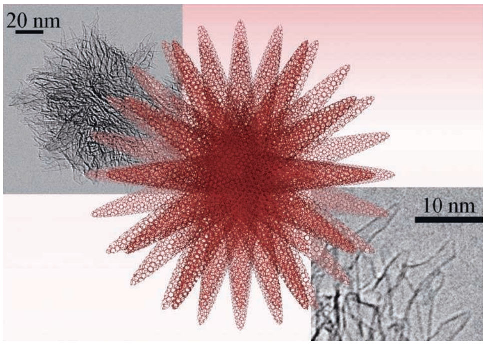
Iijima helped develop the world's first high-resolution electron microscope in the 1970s, and became one of its earliest users. Peering into the nanoscale domain for the first time, he saw an unexpected zoo of structures. There were onion-shaped carbon nanoparticles (these turned out to be fullerenes, which today are used in a number of biomedical innovations), as well as carbon needles scattered in the soot deposited on the electrodes of the arc discharge.

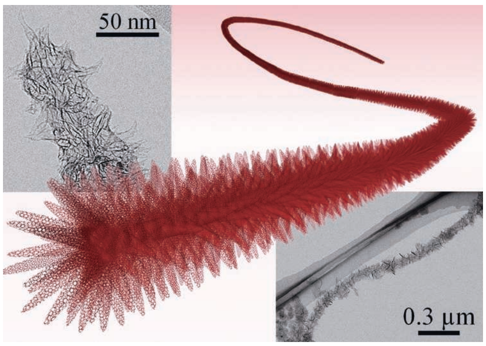
Iijima called the needles 'carbon nanotubes' (pictured opposite, at top left), after rejecting the alternative names 'NEC tubes' and 'Iijima tubes'. His 1991 paper describing the discovery has been cited an astounding 43,000 times. The new carbon structures had unprecedented strength and electrical conductivity, and together with fullerenes kicked off the new field of carbon nanostructure research.

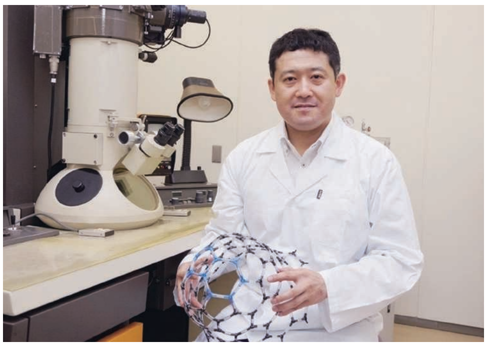
NEC researchers have since followed in Iijima's footsteps, continuing the company's tradition of leadership in carbon nanostructure research. For example, a critical problem facing the field since its inception has been the separation of metallic from semiconducting











nanotubes, which have very different electronic behaviours, but are produced as a mixture. NEC has been able to advance the use of electrophoresis to achieve a separation in excess of 98%, and recently scaled up the method, explains Dr Fumiyuki Nihey, a principal researcher at NEC. This success, he says, will boost the commercialization prospects of carbon nanotube transistors (above, top right). It has, for example, allowed Nihey and his colleagues to create patterned mats of semiconducting tubes into flexible large-area devices using low-cost printing techniques.

More opportunities for novel products have also emerged since Iijima's 1998 discovery of carbon nanohorn aggregates, where thousands of conical sheets of carbon (carbon nanohorns, pictured above, at centre left) assemble radially to form a spherical aggregate. These are attractive materials due to a high dispersibility in solutions and large specific surface area: they have the potential to be applied to energy devices such as supercapacitors or fuel cells. Large-scale production equipment for carbon nanohorns was first developed by NEC (above, at centre right).

Scientists at NEC labs have also demonstrated that there are more fascinating carbon nanostructures waiting to be discovered and exploited. Last year, Dr Ryota Yuge (above), a principal researcher at NEC, reported the discovery of the carbon nanobrush (above, at bottom left) — a structure of fibrous aggregates composed of radially assembled carbon nanohorns. The nanobrush has an unprecedented combination of electrical conductivity and the ability to disperse in solution, along with a large surface area. "This makes the carbon nanobrush a promising candidate for electrode materials in supercapacitors, electrochemical actuators, fuel cells, lithium ion batteries and sensing devices," explains Yuge.

New types of devices bring new flexibility

NEC researchers are excited by the great potential of carbon nanomaterials for completely new kinds of devices. "Consider a flexible sensor attached to a living body," says Yuge. "It can extract biometric information for health maintenance or the early detection of disease. Or think about large-area pressure sensor sheets for product management. The flexibility, high speed and durability required for devices like these can be achieved through the use of nanocarbons."

Similarly, energy devices live or die by the surface area and conductivity of their component materials. Nanocarbons are uniquely positioned to provide both, says Yuge, with immediate potential applications in lithium ion batteries, supercapacitors and fuel cells. He adds that carbon nanomaterials also offer opportunities to create devices that balance cost and performance.

As their work progresses, Yuge and Nihey draw inspiration from NEC's history of innovation. "Every researcher at NEC aims to become a pioneer of new technology," says Yuge. "It's a part of our culture." ■

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Nanotube factory springs into production

Open innovation and collaboration between industrial, academic, and government stakeholders in Japan **HAVE CULMINATED IN THE OPENING OF THE WORLD'S FIRST FACTORY** for mass manufacturing **SINGLE-WALLED CARBON NANOTUBES.**

Nearly a quarter-century ago, researchers worldwide were excited by images of tiny, single-atom thick cylinders of rolled-up carbon captured in a Japanese laboratory. These materials, quickly dubbed carbon nanotubes, were a fraction of the width of a human hair, but could be formed into stronger-than-steel bundles or into coatings with conductivity a thousand times better than copper. Despite these revolutionary properties, carbon nanotubes struggled to establish a foothold in the industrial materials sector due to complex and expensive production processes.

Now, collaboration between Zeon Corporation and Japan's National Institute of Advanced Industrial Science and Technology (AIST) has shown that nanotubes can make the leap from laboratory curiosities to consumer devices thanks to the first-ever industrial facility dedicated to producing these innovative carbon fibers on substrates as large as 50 cm^2.

Pipe dreams

Petroleum processors were among the first to discover intriguing, nanoscale forms of carbon fibers when they characterized the deposits that occasionally plugged their machinery. They, and other researchers, found evidence of extra-thin strands of graphene tubes with a variety of diameters and shapes. At these dimensions, the fibers gain sufficient surface area to turn into energy-storing supercapacitors and have remarkable thermal and mechanical stability.

Kohei Arakawa, president of Zeon Nano Technology, explains how advances in the fabrication of carbon nanofibers set the stage for the eventual high-throughput manufacturing of nanotubes. "When I started research back in 1982, the preferred method of producing nanofibers was to grow them from catalysts on substrates," he recalls. "But these techniques were patented, and my job was to search for another way."

NANOTUBES CAN MAKE THE LEAP FROM LABORATORY CURIOSITIES TO CONSUMER DEVICES

Arakawa helped develop a 'floating' catalyst made from a ring-shaped, iron-containing ferrocene molecule that sped up production rates by nearly 500 times. In this approach, ultrafine droplets of catalyst particles and reactive hydrocarbon gases such as acetylene are sprayed onto samples held in a hot furnace. The catalyst initiates fiber growth and remains embedded in the tip of the carbon thread until its natural activity gives out — yielding highly uniform coatings in the process.

"This production method really fascinated me, and I had big dreams of commercializing it," says Arakawa. "Unfortunately, my employer at the time had a different viewpoint. So I made up my mind and took a new job developing liquid crystal displays. But now, the vapour technique has been widely adapted and is the standard method of manufacturing carbon nanotubes."

Making a super-sized upgrade

In the early 2000s, AIST put together a team to explore ways of adapting vapour depositions for nanomaterial manufacturing. The researchers uncovered a game-changing development when small drops of water were incorporated into a typical nanotube synthesis. While water can sometimes 'poison' catalysts and slow their activity, the humidity exposure had the opposite effect — the water supercharged the catalytic assembly of dense forests of single-walled nanotubes, perfectly vertical and up to 2.5 mm long (top right).

Using this new 'super-growth' technique, AIST demonstrated they could deposit nanotubes onto surfaces with a record-setting purity of 99.98% and an efficiency gain of 1,000 times that of conventional methods. However, one setback remained: the substrates for nanotube growth could not be enlarged beyond a few millimetres. To fix this flaw, the research team asked Arakawa — then developing optical films at Zeon Corporation — for his insights into large-scale fabrication.

"In spite of having previously given up research into carbon nanotubes, I still understood their charm," says Arakawa. "I accepted the proposal to collaborate with AIST and by 2006 we were at work developing a continuous process for larger substrates."

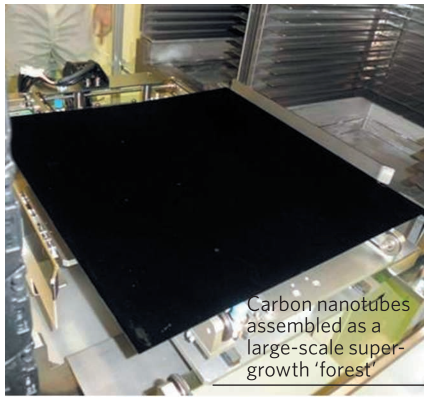
Open for business

Having recruited experts in thermal fluid simulations and catalysis, the new initiative identified several changes needed to scale up nanotube production. For instance, by using metals as deposition substrates instead of silicon wafers, the team found a shortcut that regenerated catalyst particles non-stop and avoided the need for costly reactor shutdowns. Other innovations, including optimising gas flow to improve surface coverage, eventually led to the successful fabrication of nanotube films at centimetre scales.

In November 2015, the ambitions of Zeon Corporation and AIST finally came to fruition

Carbon nanotube compounds can be used to create remarkably strong materials

Carbon nanotubes, like in this small-scale ‘forest’, can benefit a range of products



Carbon nanotubes assembled as a large-scale super-growth ‘forest’

Mass production of carbon nanotubes takes place at Zeon Corporation’s plant in Shunan, Yamaguchi prefecture

with the opening of their pioneering nanotube factory in the welcoming climate of Japan’s Seto Inland Sea.

Now Arakawa is overseeing the development of products that take advantage of the unique thermal, electrical, and mechanical properties of these nanomaterials.

“We plan to introduce a thermal interface material to the market shortly that removes heat from semiconductor chips with superb performance,” says Arakawa. “Products such as ordinary O-rings could benefit from the strength of carbon nanotubes, and venture companies are promoting these coatings for non-volatile semiconductor memory.”

Susumu Katagiri, the senior vice president of Zeon Nano Technology, notes that the company’s expertise in elastomers can help it to gain access to the projected multi-billion-dollar global market for nanotubes.

“We expect strong synergies with the carbon nanotube business, and welcome collaborators who intend to aggressively develop applications,” says Katagiri. “Meanwhile, we are still searching for ways to reduce production costs by 10 to 100 times in the coming years.” ■

ZEON

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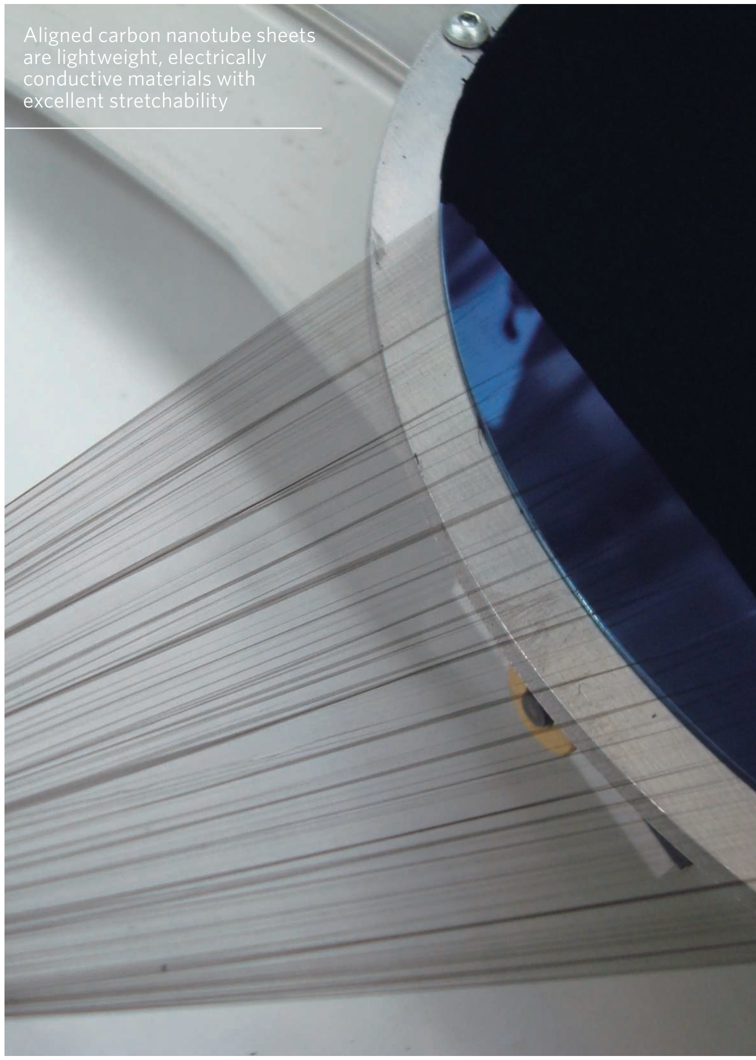


Aligned carbon nanotube sheets are lightweight, electrically conductive materials with excellent stretchability

Widening the scope of carbon nanotubes

TAIYO NIPPON SANSO CORPORATION is well established in the energy industry. Now, innovation in carbon nanotubes is leading its charge into novel applications across a range of markets.

Operating in more than 20 countries through industrial gas production facilities and subsidiaries, Taiyo Nippon Sanso Corporation is leveraging its global reach and technologies to venture into new market areas.

Since 2002, the company has strengthened its technical development to commercialize carbon nanotubes (CNT) for wide-ranging applications in the electronics, automotive and other industries.

Taiyo Nippon Sanso is the leading provider of industrial gases in Japan with a 40% share of the domestic market in 2016: the company ranked first for core products such as oxygen, nitrogen, argon, carbon dioxide and helium, and second for acetylene. Internationally, it is well known for its semiconductor manufacturing equipment and systems, particularly in Taiwan, South Korea and the United States.

THIS CONCEPT OF 'LESS IS MORE' IS HELPING THE COMPANY REACH ITS GOALS

In recent years, the company has diversified its product line-up to include hydrogen filling stations, liquid nitrogen-based refrigeration systems and cryogenic technologies, for example, for the storage of induced pluripotent stem (iPS) cells. The company also now offers its own line of innovative CNT materials.

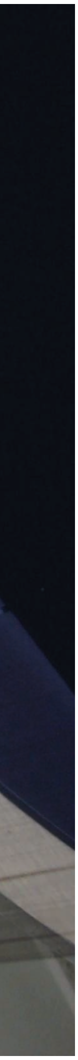
Thinking laterally for hot new products

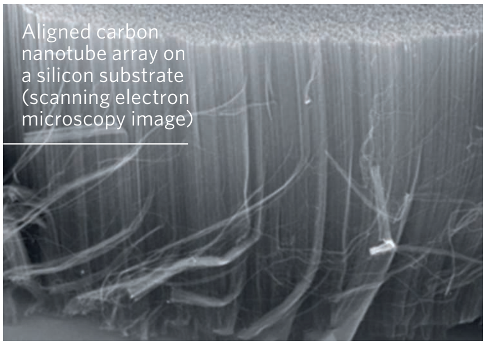
Based on its expertise in handling gas products, Taiyo Nippon Sanso's research and development laboratory in Yamanashi, central Japan, has developed a high-performing, heat-resistant material that consists of a synthetic resin (polytetrafluoroethylene or PTFE — a familiar product is Teflon®) mixed with a minimal amount (just 0.05%) of CNT.

Known as 'fluorinated resin with CNT', this material achieved a thermal conductivity 2.6 times greater than that of PTFE alone. Electrical conductivity was shown to be on par with PTFE containing 3% of conventional carbon black, used previously for automotive parts and other electrical components. Moreover, the CNT version was found to help prevent build-up of static electricity.

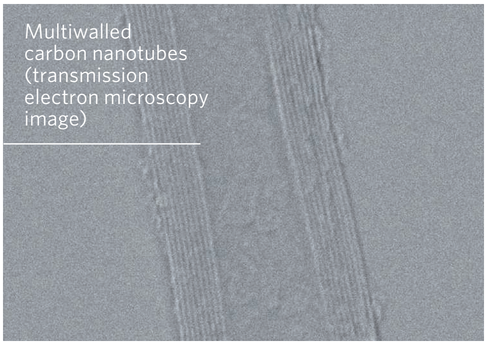
This concept of 'less is more' is helping the company reach its goals. "By minimizing the amount of CNT needed to achieve high performance, we have met our target of producing 10 tonnes of this material annually," says Toru Sakai, project manager of Taiyo Nippon Sanso's research and development planning division. "Applications so far include semiconductors, auto parts, packaging materials and pipelines for transporting chemical liquids."

The ability to tolerate solvents is important. Even when the material was immersed in hydrochloric acid aqueous solution for 24 hours, researchers at the Yamanashi laboratory found that the material remained intact: the metal and carbon components of the material were below the detection limit. Development manager Junichirou Asai says: "This is an important advantage, as it means that it can be used in cleaning equipment or in other industrial procedures where cleanliness takes precedence."

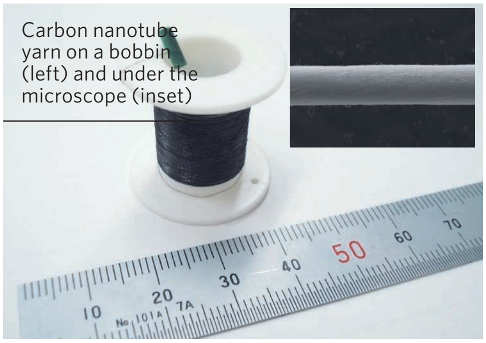




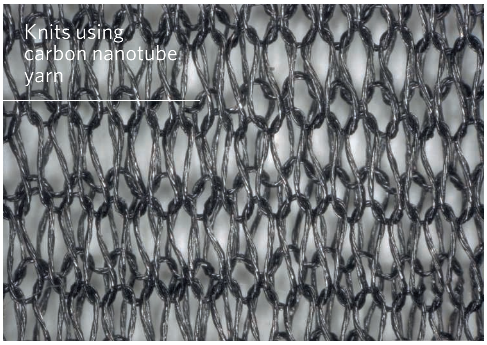
Aligned carbon nanotube array on a silicon substrate (scanning electron microscopy image)



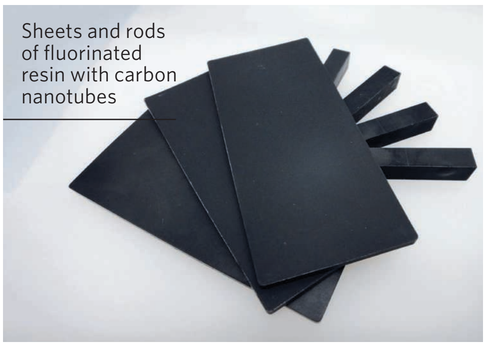
Multiwalled carbon nanotubes (transmission electron microscopy image)



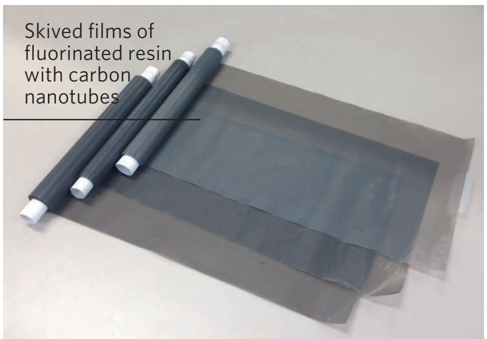
Carbon nanotube yarn on a bobbin (left) and under the microscope (inset)



Knits using carbon nanotube yarn



Sheets and rods of fluorinated resin with carbon nanotubes



Skived films of fluorinated resin with carbon nanotubes

The new material can take many forms and Taiyo Nippon Sanso currently supplies fluorinated resin with CNT as sheets, rods, tubular sleeves and skived films (used, for example, in adhesive tapes). Each shape could in future be tailored to meet the requirements of different electrical and mechanical applications. Food and biomedical applications however will require further testing.

Adding a new string to their bow

The company's nanotech innovations go still further — and finer. "We are particularly proud of our development of CNT yarn, an ultralight, durable and highly flexible thread made of 100% CNT," says Sakai. "We have already fabricated samples such as grid meshes and knitted fabrics with this yarn, which we expect will respond to new user needs."

As the crowning achievement of five years of developmental research, the CNT yarn is now at the cusp of full-scale marketability. Sakai explains that the production process involved two stages.

First, using Taiyo Nippon Sanso's proprietary technologies, carbon nanotubes with exceptionally high purity (over 99.5% CNT) and with a diameter of between 5 to 20 nm were aligned and placed as a series of layers on to a silicon substrate. These multiple layers formed a thin sheet of CNTs, known as buckypaper after the discovery of buckminsterfullerene by Nobel laureates, Robert Curl, Harold Kroto and Richard Smalley in 1985. These aligned sheets are stretchable — or what is known in the industry as 'drawable'. With a thickness ranging from 10 to 30 µm, these drawable CNTs are lightweight, electrically conductive materials.

Second, working with associate company Murata Machinery Ltd, a leading textile machinery manufacturer with its headquarters in Kyoto, the drawable CNTs were spun into spools of extremely thin CNT threads. Now available are threads of several metres in length with a diameter between 10 to 50 µm. Murata Machinery's expertise in spun-yarn technology was indispensable to producing such fine thread. The CNT yarn can achieve a conductivity of 5×10^4 siemens per metre. In future, meeting industrial requirements will require optimizing not only the length and thickness but the uniform quality of the threads. "As our CNT yarn can be fabricated into other materials, within the next few years it may be used, for example, in smart clothing or in lightweight wire harnesses," says Sakai.

An international showcase

Taiyo Nippon Sanso will showcase its CNT products at Nanotech 2018, the world's largest event for nanotechnologies, to be held at the Tokyo International Exhibition Center (Tokyo Big Sight) on 14–16 February 2018, with an anticipated 50,000 visitors.

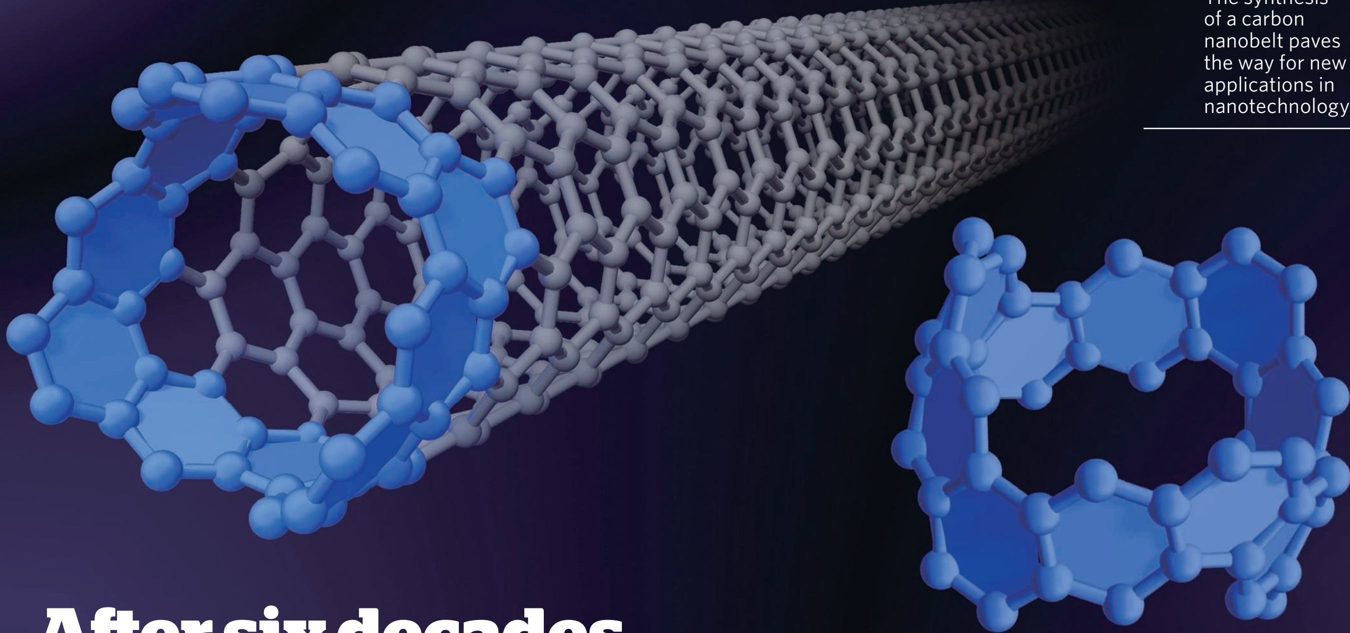
"We look forward to engaging with representatives from the semiconductor, automobile, electronics and chemical industries, and we also welcome enquiries from all those interested in our products," says Sakai. ■

CNT-uni

CNT-uni represents Taiyo Nippon Sanso's "Unique" & "Uniform" CNT product series

TAIYO NIPPON SANSO
The Gas Professionals

www.tn-sanso.co.jp/en
www.ostec-tec.info/coe-osaka/en/cnt.html



The synthesis of a carbon nanobelt paves the way for new applications in nanotechnology

After six decades of anticipation, the nanobelt has arrived

CHEMISTS HAVE SYNTHESIZED the smallest member of the carbon nanotube family.

In a way, the world of nanocarbons resembles origami — small manipulations can bring changed forms and functions. Graphene, a semi-metallic single layer of carbon atoms, is like a flat sheet of paper. Shape it into a sphere, and it becomes insulating. Wrap it into a tube, and it becomes a semiconductor that is transparent to light below a certain energy level. Twist that tube slightly, and it becomes a metal that absorbs light of all energies.

Unlike paper though, the shape of atomic-scale nanocarbons is extremely difficult to control. Lacking tools to use more direct means, scientists have had to resort to painstaking filtering techniques. To make a nanotube transistor, for example, the required semiconducting nanotubes are typically filtered from a mixture of nanostructures produced at high temperatures.

But despite decades of work, filtering remains highly imperfect. "The key issue in the field remains the preparation of well-defined materials," says Kenichiro Itami, research director of the JST-ERATO Itami Molecular Nanocarbon Project and professor of chemistry at Nagoya University.

CHEMISTS TEND TO BELIEVE THAT BEAUTIFUL STRUCTURES WILL EXHIBIT AMAZING PROPERTIES

An approach enabling more control over the shape would be a chemical synthesis of a single desired structure. Now, after an extraordinary 12 years of effort, a team of researchers led by Itami has succeeded in doing just that with one of the most sought-after nanostructures in the field — the carbon nanobelt.

Chemists have been trying to synthesize the nanobelt for over 60 years. "It's a simple and beautiful structure," says Itami, "and chemists tend to believe that beautiful structures will exhibit amazing properties."

The nanobelt consists of a thin ring of carbon atoms joined in a loop, as if someone had taken a vertical slice from the centre of a nanotube. Crucially, this means that the nanobelt can be used to grow metallic or semiconducting nanotubes with perfect fidelity — no filtration required. "In this regard," Itami says, "carbon nanobelts are the ultimate seed."

Nanobelts may also be useful in nanomachines, single-molecule electronics, photonics, and spin transport. They may even make a perfect nanocar 'tyre'. Being both the newest and the smallest well-defined member of the carbon nanotube family, many new applications may be found, says Itami. "People can't predict how it will change the game."

Scientists around the world will soon get the chance to try. Tokyo Chemical Industry Co., Ltd. (TCI) is collaborating with Nagoya University to efficiently scale up the synthesis of the nanobelt, and aims to make it commercially available within six months. Inquiries, they say, are already coming in. ■

NAGOYA UNIVERSITY

ERATO Itami Molecular Nanocarbon Project, Nagoya University

www.jst.go.jp/erato/itami

Highly conductive carbon nanotubes head to market

JAPANESE COMPANIES, BOTH NEW AND OLD, collaborate to take carbon nanotubes to an industrial scale.

Stronger but lighter than steel, carbon nanotubes are only a few billionths of a metre in diameter, but can be up to a thousandth of a metre in length. They have excellent electrical conductivity, but can also behave like a semiconductor. These attributes make them an exciting prospect for a wide variety of applications. But to realize these applications, and take them to the next level, requires an industrial-scale method to create high-quality nanotubes of controllable diameter and sufficient length. Meijo Nano Carbon and Osaka Soda, two Japanese companies with very different histories, are now working together to meet this challenge.

Enhanced direct injection pyrolytic synthesis, or eDIPS, is one possible method of synthesizing carbon nanotubes. eDIPS originated at the National Institute of Advanced Industrial Science and Technology in Japan and this method is now being further developed by the venture company established in 2005, Meijo Nano Carbon. It differs from conventional methods in that it does not grow the nanotubes on a substrate, instead adopting a type of chemical vapour deposition that uses a fine metal catalyst floating in a flowing gas.

"By optimizing the reaction using two or more carbon sources with different decomposition properties, it is possible to synthesize high-crystal-quality, single-walled carbon nanotubes," explains Takeshi Hashimoto, CEO of Meijo Nano Carbon. This approach has dual advantages — it creates nanotubes with a large electrical conductivity (a thousand times more conductive than carbon black) and it means that the distribution of nanotube diameters can be controlled.

SUCCESS IS ALREADY DEMONSTRATED IN THE DIVERSITY OF THEIR CUSTOMERS

Osaka Soda brings the expertise needed to take this process to an industrial scale. Established in 1915, Osaka Soda first produced caustic soda and chlorine gas by electrolysis of sodium chloride. Over the last century they have evolved into a company catering for the materials needs of the chemical, healthcare, biotechnology, energy and environmental business sectors. But bringing their know-how to the fabrication of carbon nanotubes will take them back to their roots.

"Carbon nanotube production requires large amounts of hydrogen gas and we can readily supply pure hydrogen by the electrolysis of sodium chloride," says Yoshiro Furukawa, director of Osaka Soda. "Therefore, we believe Osaka Soda can play an important role in scaling-up the production of carbon nanotubes to an industrial scale."

The success of MEIJO eDIPS nanotubes is already demonstrated in the diversity of their customers: from chemical manufacturers of films and resins to aerospace- and automobile-related industries. And Hashimoto and Furukawa both agree that collaborations between venture and chemical companies are the ideal route to drive this success even further. ■

meijo nano carbon

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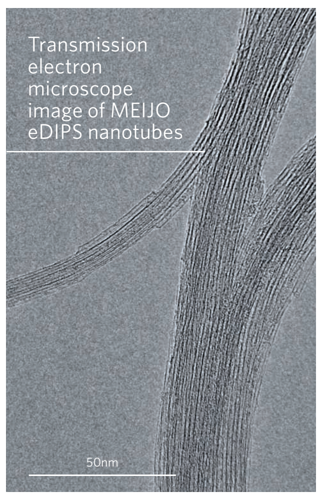
Osaka Soda's new R&D facility serves as a base for collaboration


Carbon nanotubes made by the MEIJO eDIPS method



Transmission electron microscope image of MEIJO eDIPS nanotubes

CARBON NANOTUBES SET TO INNOVATE INDUSTRY

Researchers at SHINSHU UNIVERSITY'S INSTITUTE OF CARBON SCIENCE AND TECHNOLOGY aim to advance Japanese industry with the latest innovations in nanocarbon science.

The Institute of Carbon Science and Technology (ICST) at Shinshu University holds an impressive track record in researching nanocarbon. A material that is expected to transform industrial innovation in the 21st century, nanocarbon can be integrated into polymer composites as carbon nanotube fillers. These composite materials have enhanced characteristics and advanced functions owing to their unique structure and have potential applications in a broad range of areas, including biomedicine, environment, energy, and resources.

Ever since Shinshu alumnus Morinobu Endo (pictured, far right) and colleagues developed a method to synthesize a carbon nanotube using the catalytic vapour-phase process and reported on the structure of a synthesized carbon nanotube in 1976, researchers have been looking for ways to use carbon nanotube composites in practical applications. Their strong and flexible mechanical properties combined with excellent thermoelectric characteristics make carbon nanotubes a greatly promising material, one that is anticipated to lead to new composites. However, few highly successful applications using carbon nanotubes have emerged, other than carbon nanotube composites for lithium-ion battery electrodes. In most cases, carbon nanotubes were found to have degraded the physical properties of composites because carbon nanotubes, a very thin one-dimensional substance, tend to cluster together. Although attempts have been made to homogeneously disperse carbon nanotubes using various high-energy mixers, only a few have met with success. Carbon nanotube agglomerates break into pieces when mixed with a base material using strong force. However, they are not disbanded.

THE ICST HOLDS AN IMPRESSIVE TRACK RECORD IN RESEARCHING NANOCARBON

The ICST's first successful application in this area used carbon nanotubes in an aluminum and rubber composite. Researchers at the institute sought a method to disband carbon nanotube agglomerates and found the answer: a method of mixing that incorporated the elasticity of natural rubber. The researchers found that the high elasticity of natural rubber fiberized the mixture through repeated deformation and restoration, resulting in a carbon nanotube/natural rubber composite. Toru Noguchi (pictured, first right) and colleagues discovered that pouring melted aluminum onto the carbon nanotube/natural rubber composite produced a carbon nanotube/aluminum composite. The resulting composite exhibited a high level of stiffness and heat resistance, as well as highly durable electron emissivity. In the course of investigating the structure and physical properties of the carbon nanotube/natural rubber composite, the researchers found that the fiberized carbon nanotubes formed a structure like a microscopic jungle gym in the natural rubber, which enhanced the physical properties of the composite. The institute named this phenomenon 'cellulation' and has subsequently applied cellulation technology to different kinds of rubber. Fluorocarbon rubber developed with this technology displayed remarkable durability and heat resistance. This new rubber offers practical applications for various types of sealing materials used in harsh environments. Cellulation technology also has extensive applications in automotive and other industries (prototypes are shown in the bottom image).

Since ICST researchers developed a method to increase pseudoelasticity, which can be applied to plastics with low elasticity, the industry has generated many high-performance plastics composites. These composites are expected to lead to higher functionality for recycling plastic waste, which is essential to resolving environmental problems. The institute has also applied cellulation technology to natural cellulose nanofibers—a thin material similar to carbon nanotubes—and new composites are currently under development. Carbon nanotubes and cellulose nanofibers are nano-nano composite materials that compete with and cooperate with each other, and could lead to innovative polymeric materials. The ICST looks forward to developing new innovations with these materials that will ensure Japanese industry continues to go from strength to strength. ■

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Shinshu University
Endo Lab.

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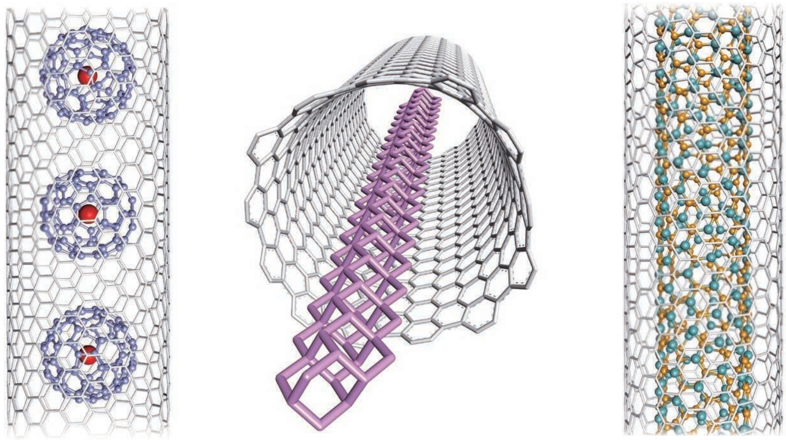
Family of nanopeapods



Designed by Yusuke NAKANISHI

PERFECTING PEAPODS

Nagoya University's Shinohara laboratory is **SPEARHEADING RESEARCH** into the tiny 'nanopeapods' made by encapsulating materials in carbon nanotubes

Not all peapods are green. With advances in nanoscience, some peapods are tiny, black and contain peas made of diamond.

The Shinohara research laboratory at Nagoya University is exploring a brand-new class of hybrid carbon nanotube material known as 'nanopeapods' or simply 'peapods'. Chemically and mechanically robust, carbon nanotubes are flexible tube-shaped materials that are electronically and thermally well-conductive and environmentally friendly, with typical diameters of 1–10 nm.

'Peapods' are made up of atoms, molecules, or nanowires of various kinds encapsulated in the internal hollow spaces of carbon nanotubes. These are of great interest since the inner space of carbon nanotubes is very special in terms of its inherent one-dimensionality and small diameter. Interestingly, many different types of atoms and molecules have so far been encapsulated inside carbon nanotubes whenever their diameters and the 'encapsulates' fit properly with each other.

When atoms, molecules or nanowires are encapsulated in carbon nanotubes, properties of the carbon nanotubes often vary due to the electronic interaction generated between carbon nanotubes and their encapsulates. For example, when metallofullerenes (fullerenes with metal inside) are doped into single-walled carbon nanotubes, a substantial electron transfer occurs from the metallofullerenes to these carbon nanotubes, resulting in the emergence of a unique phenomenon called the 'band-gap modulation' of single-walled carbon nanotubes. When this occurs, the band gaps are not uniform along the single-walled carbon nanotube axis direction compared to conventional single-walled carbon nanotubes.

The inner hollow spaces of single- or double-walled carbon nanotubes can also be regarded as 'nano test tubes' for fabrication of one-dimensional nanomaterials, which are not available when using conventional bulk synthesis. One of the best examples is the synthesis of 'diamond nanowires' in carbon nanotubes.

> **'PEAPODS' ARE MADE UP OF ATOMS, MOLECULES, OR NANOWIRES ENCAPSULATED IN THE INTERNAL HOLLOW SPACES OF CARBON NANOTUBES**

High temperature annealing of double-walled carbon nanotube peapods encapsulating a diamantane molecule ($C_{14}H_{20}$) at 870K induces the formation of so-called diamond nanowires in double-walled carbon nanotubes, in which all carbon atoms in the nanowires possess strong sp^3 bonds, as in the bulk diamond. Furthermore, single-walled boron-nitride (BN) nanotubes, which have not yet been synthesized in bulk, can easily be obtained in high yield in single-walled carbon nanotubes when ammonia-borane (NH_3BH_3) peapods are treated at high temperatures of 1,670K.

Nagoya University intends to keep at the forefront of nanopeapod research and continue exploring the inner space of carbon nanotubes and nano test tubes, an area which will be sure to tantalize physicists, chemists and material scientists for years to come. ■

NAGOYA UNIVERSITY

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