Takashi Taniguchi with his crystal-making hydraulic press at the National Institute of Materials Science in Tsukuba, Japan.

THE CRYSTAL KINGS

Two researchers in Japan supply the world's physicists with a gem that has accelerated graphene's electronics boom.

BY MARK ZASTROW

PHOTOGRAPHS BY MARK ZASTROW

The smell of acrid metal fills the air as Takashi Taniguchi reaches into the core of one of the world's most powerful hydraulic presses. This seven-metre-tall machine can squeeze carbon into diamonds — but they aren't on its menu today. Instead, Taniguchi and his colleague Kenji Watanabe are using it to grow some of the most desired gems in the world of physics.

For the past eight days, two steel anvils have been crushing a powdery mix of compounds inside the press at temperatures of more than 1,500 °C and up to 40,000 times atmospheric pressure. Now, Taniguchi has opened the machine and cooling water is dribbling from its innards. He plucks out the dripping prize, a 7-centimetre-wide cylinder, and starts chipping at its outer layers with a knife to get rid of the waste metal that had helped to regulate the pressures and temperatures. "The last steps are like cooking," he says, focusing intently on his tools. Eventually, he reveals a molybdenum capsule not much bigger than a thimble. He puts it in a vice and grasps it with a wrench the size of his forearm. With one twist, the capsule fractures and releases a burst of excess powder into the air. Still embedded inside the capsule are glimmering, clear, millimetre-sized crystals known as hexagonal boron nitride (hBN).

Materials laboratories all over the world want what Taniguchi and Watanabe are making here at the Extreme Technology Laboratory, a building on the leafy campus of the National Institute of Materials Science (NIMS) in Tsukuba, outside Tokyo. For the past decade, the Japanese pair have been the world's premier creators and suppliers of ultra-pure hBN, which they post to hundreds of research groups at no charge.

They've sacrificed much of their own research and almost all their press's running time to this task. But in doing so, they have accelerated one of the most exciting research fields in materials science: the study of

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electronic behaviour in 2D materials such as graphene, single-atom-thick sheets of carbon. These systems are thrilling physicists with fundamental insights into some of the quantum world's most exotic electronic effects, and might one day lead to applications in quantum computing and superconductivity — electricity conducted without resistance.

It's easy to make graphene itself, by using sticky tape to flake carbon layers from pencil lead (graphite). But to study the complex electronic properties of this material, researchers need to place it on an exceptional surface — a perfectly flat, protective support that won't interfere with graphene's fast-travelling electrons. That's where hBN comes in as a transparent under-layer, or substrate. "As far as we've investigated, that is the most ideal substrate for hosting graphene or other 2D devices," says Cory Dean, a condensed-matter physicist at Columbia University in New York City who was part of the team that first worked out how to pair hBN and graphene. "It just protects graphene from the environment in a beautiful way."

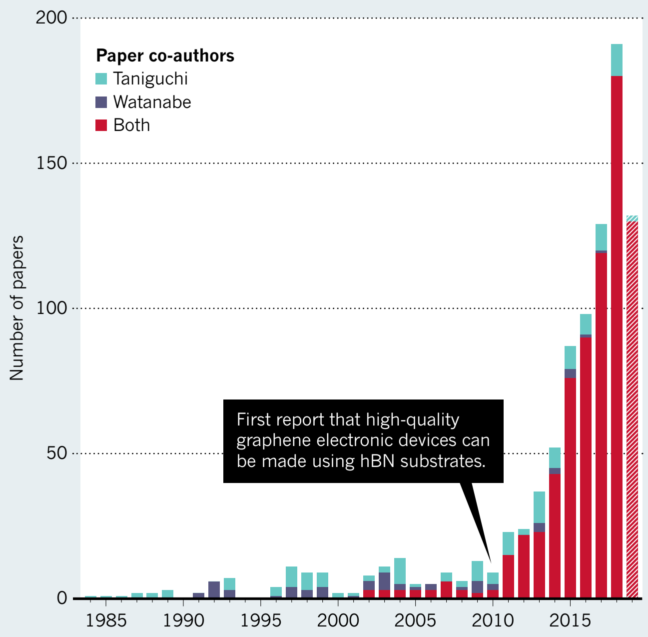
When a flake of hBN comes into contact with graphene, it can also act like cling film, making it possible to precisely pull up the carbon sheet and place it back down. That allows researchers to create devices by stacking multiple layers of 2D materials, like a sandwich (see 'Graphene sandwich').

Since last year, for instance, materials scientists have been buzzing about the finding that simply by misaligning two sheets of graphene by precisely 1.1 ° — a 'magic angle' — the material can become a superconductor at very low temperatures[1,2]. And in July, researchers reported signs of superconductivity when three sheets of graphene are stacked atop each other — no twisting needed[3]. These research studies, like hundreds of others, all used slivers of Taniguchi and Watanabe's hBN to protect their samples. "We are just involved," Taniguchi says modestly. "It is a sort of by-product for us." Dean is more effusive about the pair's hBN: "It's really the unsung hero of the process," he says. "It's everywhere."

Neither Taniguchi nor Watanabe is a graphene researcher, and they had no idea that their gems would become so desirable. The researchers now have several patents related to their hBN-making process, but say they don't expect to be able to commercialize it — at the moment, only research groups need the highest-purity crystals. There is a sizeable perk, however. Because the pair are credited with authorship on studies using their crystals, they have become among the world's most-published researchers. Together, Taniguchi and Watanabe appeared as authors on 180 papers last year — and, since 2011, they have co-authored 52 papers in *Science* and *Nature*, making them the most prolific researchers in these journals over the past 8 years (see 'Crystals in demand').

CRYSTALS IN DEMAND

Takashi Taniguchi and Kenji Watanabe have co-authored hundreds of papers by supplying crystals of hexagonal boron nitride (hBN) to physics laboratories around the world.



First report that high-quality graphene electronic devices can be made using hBN substrates.

SOURCE: SCOPUS/NATURE

Their crystal empire might not last forever: Taniguchi is edging towards retirement age, and other research groups are trying to make high-quality hBN, which could help improve the supply and speed up research. But for now, physicists are somewhat reluctant to test unproven samples when they know the NIMS ones work so well, says Philip Kim, a leading condensed-matter physicist at Harvard University in Cambridge, Massachusetts. "Why Watanabe and Taniguchi? Because their crystal is the best."

UNDER PRESSURE

The massive hydraulic press lives in a cavernous industrial space at the Tsukuba laboratory, which is filled with the continuous hum of machinery and light that streams in from high windows, casting dusty rays across the equipment below. The machine was built between 1982 and 1984, when the laboratory was a part of the National Institute for Research in Inorganic Materials (NIRIM), one of NIMS' forerunners. Taniguchi arrived five years later, after leaving a postdoctoral position at the Tokyo Institute of Technology. The press was originally designed to make diamonds, but in the 1990s, Japan's government embarked on a research programme dubbed 'Beyond Diamond' to find the next big thing in ultra-hard materials, potentially for cutting substances or for use in semiconductors.

One of the programme's leading candidates was boron nitride in its cubic crystal form (cBN) — a dense structure in which boron and nitrogen atoms are arrayed like the carbon atoms in diamond. Taniguchi initially focused on growing ultra-pure cBN in the press — but his group couldn't eliminate impurities, stray bits of carbon and oxygen that intruded when the samples were being prepared, and so the crystals came out with an unwanted dull, brownish cast. As a by-product, however, the process produced clear hBN, in which layers of hexagonally arrayed atoms slide easily over each other, analogous to the carbon layers in graphite.

Watanabe, a materials scientist and spectroscopist, joined NIRIM in 1994, just as the Beyond Diamond programme was starting. He spent a few years studying the optical properties of diamonds. But amid an institute-wide push for cross-disciplinary collaboration in 2001, Taniguchi knocked on Watanabe's door and invited him to take a look at his cBN crystals.

The two researchers have contrasting styles. Taniguchi is known for his parties, blasts the music of Queen through the lab as he runs the press late at night and, even at the age of 60, still plays soccer with his colleagues at lunchtime. Watanabe, three years younger, is soft-spoken, detail-oriented and prefers tennis. But the scientists worked well together and published their first paper[4] on cBN crystals in 2002.

A year later, Watanabe, complaining about the quality of the cBN Taniguchi was passing to him, took a look at a box of discards from the press. The hBN crystals caught his attention, and he decided to examine their properties. Taniguchi was sceptical: "I said, 'This is hBN — the boring stuff!'" Watanabe, however, discovered something new: the hBN luminesced under ultraviolet light — unlike the diamond or cBN he had been looking at for years. "It was the most exciting moment of my career," he says — a finding that left him buzzing for weeks afterwards. The pair reported that result in May 2004, proposing that hBN could be a promising crystal for UV lasers[5].

Later that year, a preprint began circulating from physicist Andre Geim and his team at the University of Manchester, UK[6]. They had successfully isolated single-atom layers of graphene, kicking off the craze for atomically thin 2D materials. The frenzy of activity was something Taniguchi and Watanabe observed with curiosity. "We had no idea about 2D materials," says Taniguchi. But half a decade later, 2D materials researchers would find out about them.

AN EYE-POPPING DISCOVERY

In 2009, the graphene field was running into a problem. In theory, the material was remarkable, but researchers were struggling to realize its full potential. The problem seemed to be that graphene, being a single atom thick, conforms to the shape of whatever surface it is placed on.

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Kenji Watanabe prepares hexagonal boron nitride (hBN) crystals (left); stacks of plastic trays holding hBN pile up for posting around the world.

The flatness that makes the material unique is lost if this substrate is not equally flat. Also, because graphene is so thin, electrons travelling through it are, essentially, in contact with the substrate it rests on. That means the substrate needs to be incredibly pure: any impurities will cause the electrons to scatter, reducing electron mobility. The standard silicon oxide substrates weren't good enough, and seemed to be limiting graphene's performance.

James Hone, a mechanical engineer at Columbia University, and his then-postdoc Cory Dean had a better substrate in mind: hBN. It is atomically flat, plus it has a wide bandgap — that is, a large energy barrier that prevents electrons bound to atoms from jumping into a mobile, conductive state. That makes hBN a good insulator.

> *"Over the years, we tried four or five other sources of hBN and they were all rubbish."*

By chance, another of Hone's postdocs, Changgu Lee, had some experience with the stuff. He was studying the mechanical and electrical properties of 2D materials, and had already sourced hBN samples from a commercial firm that made hBN for the cosmetics industry; some eyeliners are up to 25% boron nitride. One day, as the three sat outside the department building eating sandwiches, Hone suggested that Lee give Dean some of his hBN so that Dean could try using it as a graphene substrate. Lee was happy to, but added that he had read in the literature about a potentially higher-quality option: the larger, purer hBN crystals produced at NIMS by Taniguchi and Watanabe. There was just one problem: he'd contacted them before, but communications had dried up. Hone suggested asking Philip Kim — "the most famous guy in graphene", as Lee says, and a faculty member at Columbia at the time — to write a request for them.

This worked, and Kim, Lee and Dean became the first outside users of the NIMS crystals for graphene research. It took Dean a year, collaborating with PhD students Andrea Young and Inanc Meric, to work out how to consistently manoeuvre graphene and hBN flakes into contact with each other. But the results were stunning. Resting on the NIMS hBN samples, the graphene's roughness was reduced by two-thirds when compared with graphene on a silicon oxide substrate — and the electron mobility was 10 to 100 times better.

The team presented their findings at the annual Graphene Week conference in April 2010 at the University of Maryland in College Park — and "everybody's eyes popped", says Kim. "It was a sensation." Instantly, everyone wanted to know how to get the hBN — including Geim, who shared the Nobel Prize in Physics that year for his work on graphene. He e-mailed Kim with one question: "Philip: what is the source?"

Taniguchi and Watanabe were suddenly inundated with enquiries and requests for samples. But when Geim, a competitor to Kim, asked them, they hesitated to reply. "Things could have become complicated," says Taniguchi. "We made the crystal — they found the property." He asked Kim: would it be okay to supply other groups — including their direct competitors? "Of course," said Kim. "A small research group at Columbia should not monopolize your crystal," Taniguchi recalls him saying.

COLLABORATION ALL AROUND

Today, Taniguchi and Watanabe have agreements to supply more than 210 institutions around the world. Taniguchi preps the crystals for posting in an office on the perimeter of the lab, where stacks of clear plastic trays holding batches of samples are scattered around microscopes on a counter. Taniguchi's current batch is number 942 — the latest in his records, which go back over a decade. The total weight of crystals in each package — holding four different samples from four runs of the press — is roughly one gram. But that can keep an entire research group going for a year.

Taniguchi and Watanabe don't explicitly ask to be full co-authors on papers, they say. To receive the samples, users sign a materials-transfer agreement with NIMS. Many researchers say the pair's co-authorship status reflects the importance of sample growers in the field. "Without their samples, without their involvement, I don't think that what we are doing can be done at this point, so sharing the authorships is really well-deserved," says Kim.

The worst part of the supply operation is the paperwork, says Watanabe. "It's a hard burden — very heavy," he says. Authors at NIMS have to file individual reports with their supervisors when they submit a paper, when it's accepted and when it's published. Watanabe, the junior

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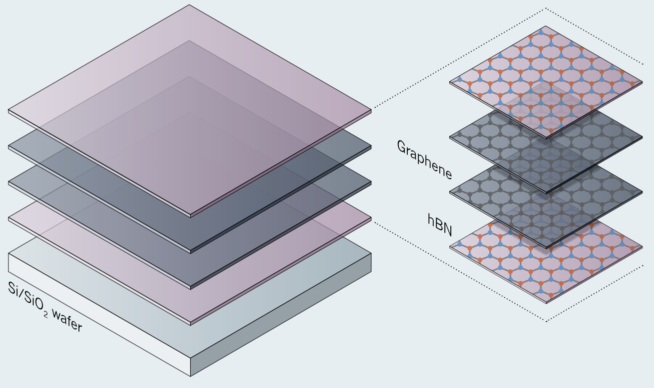
GRAPHENE SANDWICH

Graphene researchers wrap their materials in flat layers of hexagonal boron nitride (hBN). (Note this is a simplified diagram: equipment to control and measure electric fields in graphene is not shown.)



partner and the more detail-oriented of the two, takes on the task. He uses an app on his laptop to keep track of the pair's articles and preprints, which now number more than 700.

In most studies, Taniguchi and Watanabe's interaction is limited to supplying the crystals and, they hope, getting feedback from those groups on the crystal quality. Not everyone takes the time to write back, says Taniguchi, to his disappointment. But their work with the members of the original Columbia group — and the second-generation groups that the former Columbia students launched when they established their own labs elsewhere — remains a true collaboration. "They have been phenomenal partners in this process," says Dean. "They've worked with us to both provide boron nitride but also to try to figure out how to make things cleaner and make a variety of things that are interesting to us."

After the 2010 Graphene Week presentation, for instance, a postdoctoral researcher in Kim's lab named Pablo Jarillo-Herrero was the first person to ask the Japanese pair for crystals. He now leads the team at the Massachusetts Institute of Technology in Cambridge that reported superconductivity last year in twisted double layers of graphene[1,2] — a configuration protected by two layers of Taniguchi and Watanabe's hBN. And when physicist Rebeca Ribeiro-Palau moved from Dean's group in 2017 to lead her own team at the Centre for Nanoscience and Nanotechnology in Palaiseau, France, she immediately got in touch with the Japanese pair. "Making a collaboration with them was the first step, before even opening the lab," she says.

Graphene isn't the only 2D material to benefit from hBN, Ribeiro-Palau adds. Layers of more-complex materials called transition-metal dichalcogenides, for example, have also been stacked and twisted to modify their electronic properties, something that again requires hBN[7]. "It's exactly what you need to encapsulate the materials, to protect them, to give different properties, to change the spacing between layers. We use boron nitride for almost everything," Ribeiro-Palau says.

There are increasing hints that hBN can take on more than a supporting role in such devices. Aligning hBN's hexagonal structure with one of the layers in twisted graphene can break the symmetry of the graphene sheets, altering the way electrons interact, according to separate preprints reported this year from teams led, respectively, by David Goldhaber–Gordon at Stanford University in California and Andrea Young, now at the University of California, Santa Barbara[8,9].

Hexagonal boron nitride is also becoming recognized as a fascinating 2D material in its own right. Bathed in infrared light, hBN acts as a hyperlens: it can focus light and create images sharper than classical physics allows. And it has potential as a material that can emit single photons — a useful function for quantum cryptography[10]. Watanabe's finding that the material could be useful as a UV laser still receives attention, and his primary research goal remains working out how this happens.

Some of this work is done using hBN grown by methods that produce lower-quality samples, such as depositing the crystal in a thin film from a chemical vapour, which doesn't require high pressures. But for graphene researchers, Taniguchi and Watanabe's crystals remain the ones of choice. "Over the years, we tried four or five other sources of hBN and they were all rubbish," says Geim. With high-purity hBN in short supply, that hinders progress in global graphene research, he says.

Other teams are starting to catch up. A group led by chemical engineer James Edgar at Kansas State University in Manhattan has now come close to achieving the quality needed to rival Taniguchi and Watanabe's process, notes Geim. Edgar says it's not easy to duplicate the Japanese team's work because they have an expensive, giant press. But his samples, made by a simpler — and much cheaper — process involving a furnace fed with boron nitride and a nickel–chromium solvent in powder form, are "as good or nearly as good" for graphene research purposes, he says. However, they currently have ten times more crystal defects, or imperfections, in their structure.

Taniguchi, for his part, relishes the prospect of challengers to their crown, and the chance to push each other to grow purer and more perfect crystals. "We're fighting to improve our systems," he says, "but we need many collaborators — and also competitors."

A CAREER GROWING CRYSTALS

This July, Taniguchi turned 60 — the age at which researchers retire at NIMS. That was a concern for Kim. "I told him, 'Hey, Takashi, the entire 2D research field is in danger now. So we should do something!'" Luckily for the 2D field, NIMS granted Taniguchi a reprieve: earlier this year, they promoted him to a fellow position, which allows him to work until 65. He hasn't developed a succession plan yet, or identified a protégé.

For now, he continues to run the press alone. Back in his lab, he prepares the next batch — number 943 — filling a fresh thimble-sized capsule with white discs of boron nitride the size of breath mints. In between, he places a layer of barium nitride and other barium compounds, which dissolve along with the boron nitride and act as a solvent and catalyst to aid the crystal's growth and absorb impurities.

Taniguchi is cagey about the exact recipe: this is his secret sauce, and he likes to change the composition of the barium layer from batch to batch. "Using the same recipe every time is not that fun," he says. For first-time users, he'll send some baseline crystals, but with long-time users, he wants feedback on each slight change to the process. By measuring electron mobility in graphene, they can detect impurities in the underlying hBN with more sensitivity than Taniguchi and Watanabe can measure. At first, no one had any complaints about their crystals. Only in the past two years, Taniguchi says, have researchers begun reporting impurities that affect their results — a result of them pushing the limits of the material. And that motivates Taniguchi to improve. "I'm a crystal grower," he says proudly.

He clambers up over the press platform, crouching down in the jaws of the machine to place the new capsule. Back to the controls: a few button presses, and the lower anvil begins rising from the floor to hit the core. As a red digital readout counts down the distance, Taniguchi wipes some grime off the console with a tissue.

Despite decades of work growing crystals in the press, there is still much to uncover about the fundamental physics of how the process works, he says. What actually happens inside that capsule when the press clamps down remains a mystery. "Nobody knows how to measure it, how to think about what's happening, how the crystal grows. It's just imagination." ■

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CORRECTION

The News Feature 'The crystal kings' (*Nature* **572**, 429–432; 2019) erred in saying that Pablo Jarillo-Herrero was a graduate student of Philip Kim. He was a postdoctoral fellow.

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