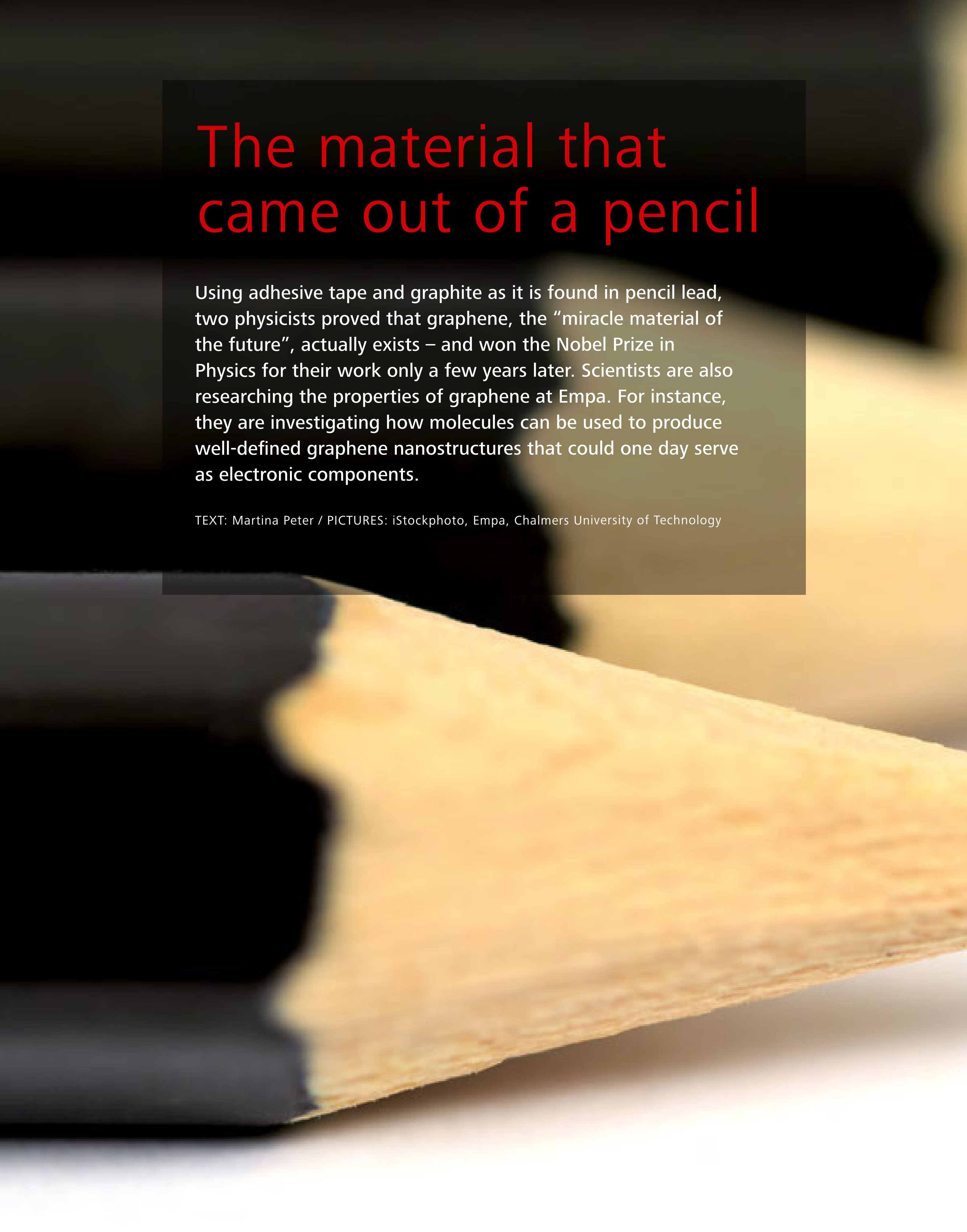
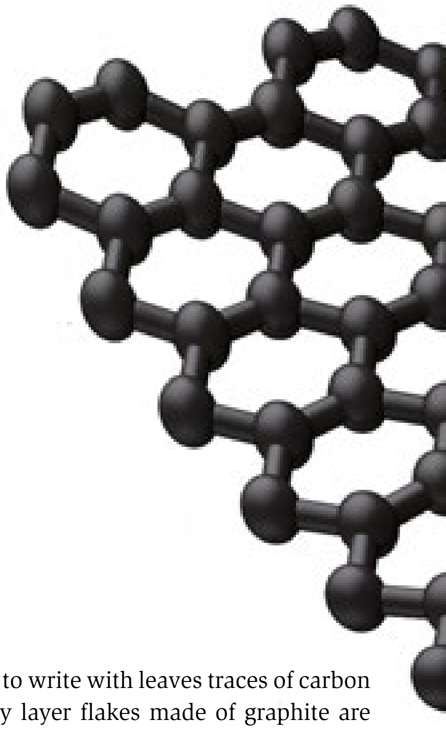
# The material that came out of a pencil

Using adhesive tape and graphite as it is found in pencil lead, two physicists proved that graphene, the “miracle material of the future”, actually exists – and won the Nobel Prize in Physics for their work only a few years later. Scientists are also researching the properties of graphene at Empa. For instance, they are investigating how molecules can be used to produce well-defined graphene nanostructures that could one day serve as electronic components.

TEXT: Martina Peter / PICTURES: iStockphoto, Empa, Chalmers University of Technology





Anyone who uses a pencil to write with leaves traces of carbon behind. In doing so, tiny layer flakes made of graphite are rubbed off the pencil lead. If you were to continue this process and wear the layers down to the last atomic layer, you would hit graphene. After all, graphite – i.e. the pencil lead – is merely graphene layers stacked on top of each other a million times over. What is surprising, however: the graphene related to conventional pencil lead turns out to be a material with extraordinary properties. It is as hard as a diamond but flexible, an excellent conductor of heat and electricity, ultra-light, tear-proof and virtually transparent – a material that could one day be used for a vast range of applications in the fields of electronics, communication technology, power generation and storage, vehicle construction and many more. And its research has set its sights on a multi-billion-Euro EU “flagship” project over the next few years.

**Graphene actually exists: simple yet ingenious proof**

Until 2004, it was inconceivable for science that a monoatomic, two-dimensional layer like graphene could actually exist under normal conditions. The belief was that such an entity would spontaneously disintegrate – until two scientists from the University of Man-

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chester reported an incredible discovery in the journal Science. Konstantin Novoselov and Andre Geim demonstrated how they had produced graphene very easily. Using simple adhesive tape, they had worn away material from a graphite surface until it only consisted of tiny, transparent flakes. In order to render these visible, the researchers stuck the tape to a silicon plate and transferred the flakes onto it. Illuminated with UV light, the flakes reflected onto the plate in a different color to the surroundings. Sure enough, as the examination of the samples with the atomic force microscope (AFM) revealed, it was graphene – monoatomic layers of carbon atoms, arranged in a honeycomb-like, extremely stable structure. In 2010 Novoselov and Geim were awarded the Nobel Prize in Physics for their ground-breaking discovery.

With the publication of their article, Geim and Novoselov sparked great enthusiasm in the scientific community. Numerous research teams began to focus on graphene and industry pricked up its ears. As the adhesive tape method was not suitable for production on an industrial scale, other methods were sought to obtain graphene. Many were based on the so-called top-down approach: individual graphene layers

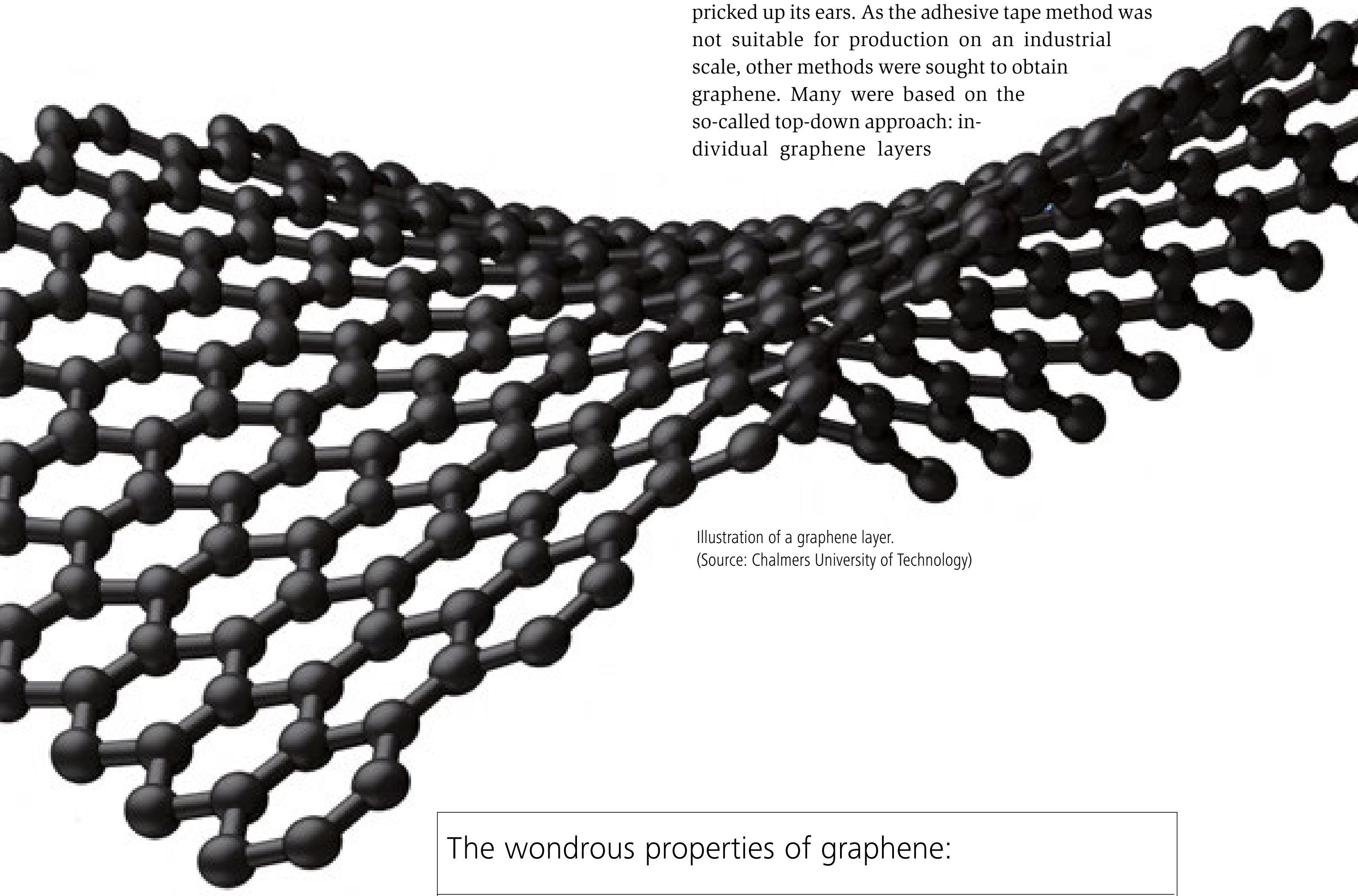


Illustration of a graphene layer.
(Source: Chalmers University of Technology)

## The wondrous properties of graphene:

- is 300,000 times thinner than a sheet of paper.
- is ultra-light; 1 square kilometer of graphene only weighs approx. 250 g.
- is the most mechanically robust material ever measured.
- is extremely flexible; it can be stretched up to 20 % without tearing.
- is virtually transparent.
- is impermeable for all gases.
- conducts heat extremely well; the material has more than twice as much thermal conductivity as a thin copper layer.
- also conducts electricity extremely well; electrons move up to 200-times faster in it than in silicon.
- has the largest specific surface measured to date – one gram has a surface of approximately 1.5 soccer fields.

are separated from graphite through chemical exfoliation – much like how Novoselov and Geim had demonstrated with their adhesive tape method. Other groups demonstrated that graphene can be deposited on catalytic copper using the classic chemical vapor deposition technique. Only last year, Sony presented a graphene film that was over 100 meters long and 21 centimeters wide.

### Miniscule electronic components

Graphene's extremely high conductivity and subsequent low dissipation power is especially intriguing for researchers who deal with electronic components. As components become increasingly smaller, the traditional use of silicon as a semiconductor material is gradually reaching its physical limits. Reliable components on a nanometer scale are right at the top of the wish list in the electronics world. Would graphene make a good substitute for silicon and Co.? Of course, the scientists from Empa's nanotech@surfaces lab headed by Roman Fasel, an adjunct professor of physical chemistry at the University of Berne, are convinced. However, only if a way can be found to temporarily halt the extremely high electrical conductivity of graphene as well. After all, electronic switches also need to be able to turn off the current, which isn't really possible with graphene because, as a semimetal, it lacks the necessary electronic band gap – the energy range where no electrons can be located.

As scientists were aware from theoretical considerations, unlike large-scale graphene layers, extremely narrow graphene ribbons exhibit the required band gap thanks to quantum mechanical effects. So graphene does make a suitable semiconductor – at least in theory. But how can such narrow graphene ribbons, merely a few nanometers wide, be produced?

Researchers had already conducted experiments using top-down methods: they used lithographic techniques to cut out narrow ribbons from a graphene layer. However, it soon became apparent that the state of the edges was also crucial for the graphene ribbon's properties. Cutting a graphene layer produces frayed, irregular edges. In order to achieve the desired electronic properties predicted in theory, the edges need to be perfectly regular. But how could this be accomplished?

### Grow it from molecules then

In 2010 Fasel's team joined forces with chemists under Klaus Müllen from the Max Planck Institute for Polymer Research in Mainz and succeeded in producing graphene ribbons that were only a few nanometers wide and had precisely defined edges. In doing so, they opted for a bottom-up approach: they grew the ribbons specifically from carefully selected precursor molecules on metal surfaces and were able to demonstrate that the narrower the ribbons, the greater the band gap – exactly as the theory predicts. The trick was to find the right molecules to grow into well-defined graphene structures on surfaces. Simulations on Empa's supercomputer "Ipazia" helped the researchers to identify the optimal growth conditions.

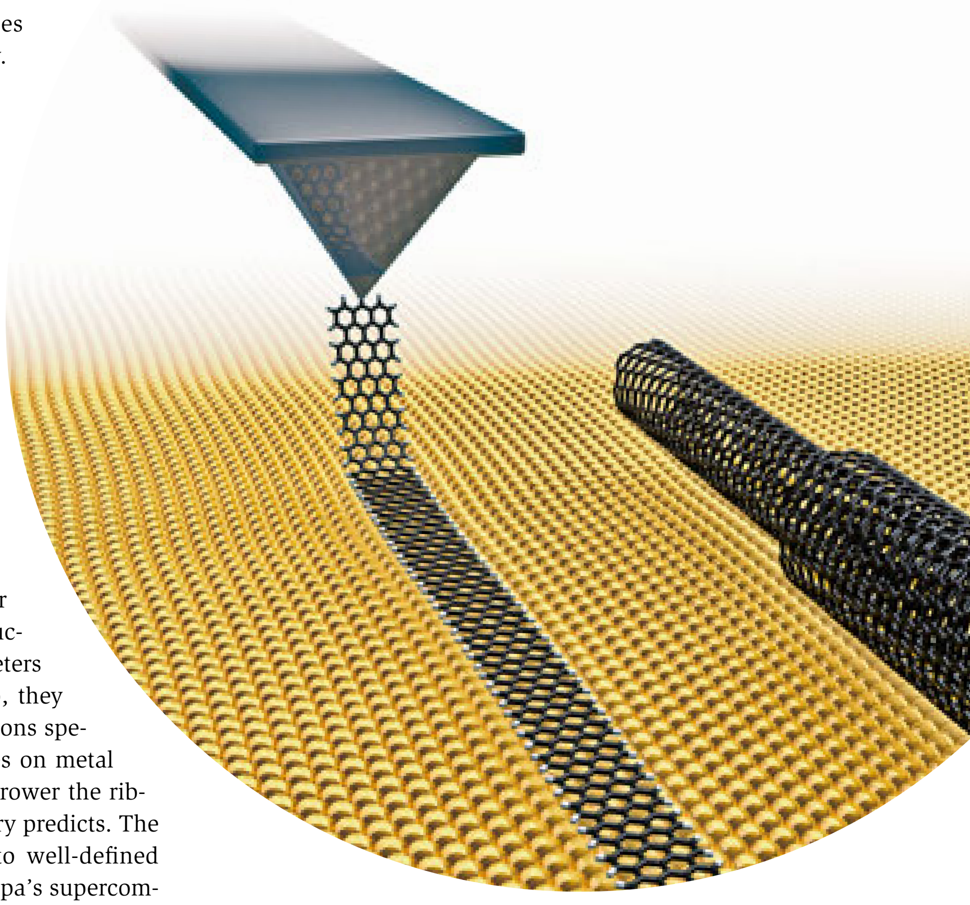
Through repeated rounds of computer simulations and experiments, coupled with measurements of the electronic properties on the scanning tunneling microscope (STM), the Empa researchers eventually managed to perfect the production processes. Using mo-

## Transferring graphene to other bases

While they were at it, the Empa scientists also solved another problem: how to integrate graphene-based nanocomponents in the conventional, primarily silicon-based semiconductor industry. Or to put it more specifically: how do you transfer ultrathin graphene ribbons from the gold substrate they "grew" upon to another – non-conductive – surface? After all, graphene components on a metal surface can't be used as electronic switches. Gold, of course, conducts electricity and creates a short circuit, which "sabotages" the interesting semiconducting properties of the graphene ribbon. Roman Fasel's team and colleagues from the Max Planck Institute for Polymer Research in Mainz succeeded in demonstrating that graphene ribbons can be transferred intact to (virtually) any substrate through a relatively simple etching process.

**Graphene nanoribbon heterojunctions, J Cai, CA Pignedoli, L Talirz, P Ruffieux, H Söde, L Liang, V Meunier, R Berger, R Li, X Feng, K Müllen, R Fasel, Nature Nanotechnology, 2014, doi.org/10.1038/nnano.2014.184**

Conductivity measurement on a graphene ribbon (left) and a carbon nanotube (right): the carbon nanostructures are lifted up with the tip of a scanning tunneling microscope (STM), enabling the current flowing through the structure to be measured.



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lecular “Lego”, they constructed graphene ribbons of different widths with different edges: zigzagged or coves lined up next to each other that were reminiscent of armchairs.

But that wasn’t all: by incorporating atoms other than carbon such as nitrogen at precisely defined positions within the graphene ribbons, Fasel and Co. were able to influence their electronic properties even further, as they recently described in Nature Nanotechnology. If “normal” and nitrogen-doped segments are lined up on a gold surface, for instance, so-called heterojunctions form between the individual segments. The researchers were able to demonstrate that these exhibited similar properties, like a classic p-n-junction – i.e. a junction from a region of positive charges in a semiconductor crystal to one of negative charges. In other words, the structural basis for numerous components in the semiconductor industry.

Apart from the width of the ribbons, the researchers are now able to set the nitrogen doping specifically, too. This means that there are now two “knobs” that the researchers can turn to influence the electronic properties of graphene nanoribbons. The Empa researchers’ work has already created quite a stir among the experts. It offers materials scientists and electrical engineers “tremendous scope to induce properties on demand,”

## Carbon nanotubes can also be produced from precursor molecules

The promising experiments using customized graphene nanoribbons have quite a history at Empa. Over ten years ago, a team of researchers headed by Pierangelo Gröning already attempted to use carbon nanostructures, so-called carbon nanotubes (CNTs), for electronic applications. “The problem back then,” describes Gröning, “was that there are dozens of types of CNT that all differ more or less electronically. In 2000 we didn’t see how it could be possible to produce a well-defined type of CNT in a pure form.” Following the successes with the molecular “flat-pack” of graphene nanoribbons, the Empa researchers were convinced that it also had to be fundamentally possible to “grow” CNTs in a controlled manner from suitable precursor molecules. They obtained the necessary molecules – planar polycyclical aromatic hydrocarbons – from Konstantin Amsharov and Martin Jansen from the Max Planck Institute for Solid State Research in Stuttgart, who had already entertained the idea of synthesizing CNTs from precursor molecules for some time.

Together, the researchers succeeded in transforming the planar molecules into a three-dimensional “cap”, the germling – much like how a solid entity begins to take shape from a sheet of paper in origami. In a second step, they added additional carbon atoms, like in classic CNT synthesis, which adhered to the open edge between the cap and the surface. As a consequence, the tube gradually grew upwards. The trick: the atomic structure of the CNT and thus its electronic properties are exclusively determined by the original germling, which is how the researchers actually managed to make pure CNTs for the first time. In August 2014 the project even made it onto the cover of the renowned science journal Nature. In expert circles, the results were already hailed as the long overdue breakthrough in the development of structurally pure nanotubes shortly after they were published. As James Tour, a chemist at Rice University in Houston, who hailed it as “a stellar breakthrough“, noted in Nature: “To those who have worked in this field for the past two decades, it is humbling to think that the selective growth of these diminutive structures has taken so long. But it is comforting to see it done so definitively.”

wrote Hinran Wang, Head of the National Laboratory of Solid State Microstructures at the University of Nanjing, China, in the November issue of Nature Nanotechnology.

### Also suitable for sensors or photovoltaics

Apart from electronic components, graphene ribbons could also be just the ticket for building highly sensitive sensors. After all, graphene ribbons respond extremely sensitively to their surroundings – their electronic properties change significantly when foreign molecules adhere to them. And photovoltaic elements could even be based on graphene one day, as Pascal Ruffieux – also from the Empa's nanotech@surfaces lab – and his colleagues recently discovered. They had noticed that especially narrow graphene ribbons absorbed visible light extremely well and thus made ideal absorber layers in organic solar cells. Unlike "normal" graphene, which absorbs light equally well on all wavelengths, the researchers were able to massively increase the light absorption in graphene nanoribbons for certain wavelengths by "setting" the precise width of the graphene ribbons atomically.

The use of graphene ribbons in the electronics world won't happen overnight, however, says Fasel. This is due to problems with upscaling to an industrial scale or replacing established, conventional, silicon-based electronics. Fasel estimates that it might take ten to 15 years for the first electronic switches made of graphene ribbons to be used in a commercial product. Nonetheless, Fasel's collaboration with BASF, which has already lasts a number of years and yielded six patents so far, just goes to show that they don't only conduct basic research.

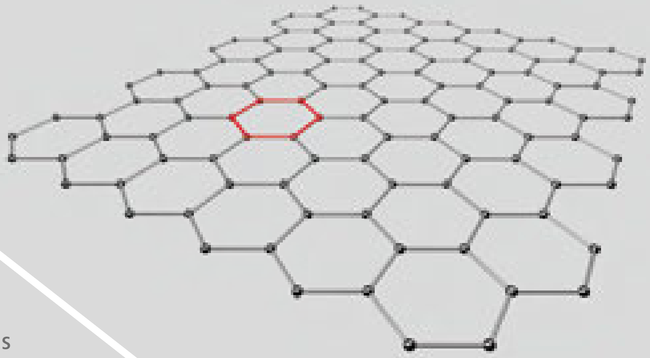
Graphene is also in demand elsewhere. The budgets for industrial research projects were increased all over the world. Moreover, the EU is looking to encourage an industrial breakthrough in the next ten years by investing half a billion Euros in the flagship project "Graphene" to co-fund projects up to 50 percent all over Europe. 142 academic and industrial research groups from 23 countries are involved, including six Swiss institutes – ETH Zurich, ETH Lausanne, the Universities of Zurich, Basel and Geneva, and Empa. Empa's studies on graphene were funded by the Swiss National Science Foundation, the State Secretariat for Education, Research and Innovation (COST action NanoTP), the US Office of Naval Research, the European Science Foundation, and BASF. //

**Exciton-dominated optical response of ultra-narrow graphene nanoribbons, R Denk, M Hohage, P Zeppenfeld, J Cai, CA Pignedoli, H Söde, R Fasel, X Feng, K Müllen, S Wang, D Prezzi, A Ferretti, A Ruini, E Molinari, P Ruffieux, Nature Communications, 2014, doi.org/10.1038/ncomms5253**

Controlled Synthesis of Single-Chirality Carbon Nanotubes, JR Sanchez-Valencia, T Dienel, O Gröning, I Shorubalko, A Mueller, M Jansen, K Amsharov, P Ruffieux, R Fasel, Nature, 2014, doi.org/10.1038/nature13607

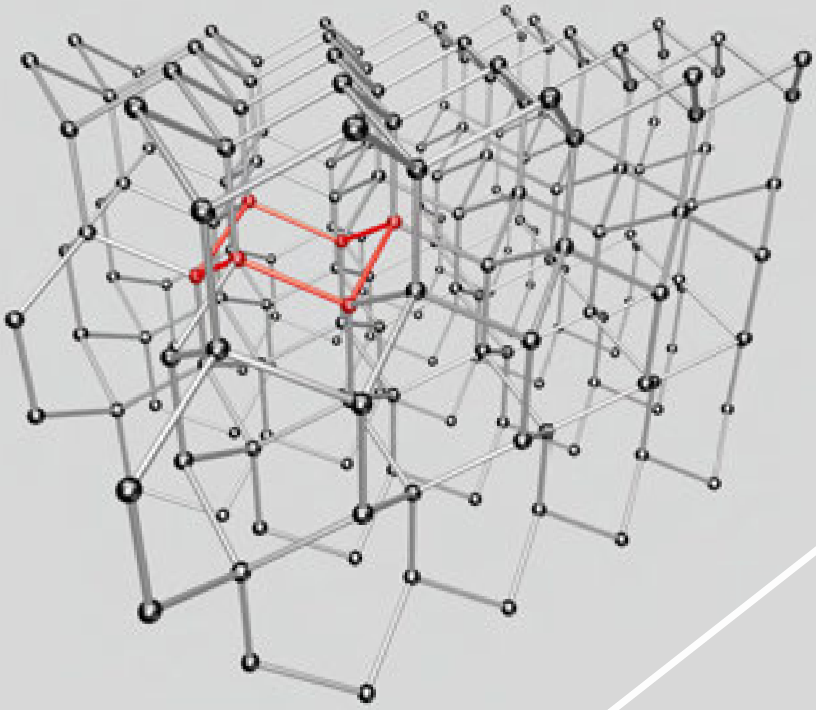
## Graphene

A single, isolated graphite layer, only one atomic layer thick (or, better, thin), is referred to as graphene. The carbon is also found in the $sp^2$ configuration. Graphene was first produced using the top-down method, which involved separating individual layers of graphite. With the bottom-up approach also developed at Empa, however, graphene ribbons that are merely a few nanometers wide and have precisely structured edges can be synthesized, giving graphene clearly defined electronic properties.



## Lonsdaleite

Lonsdaleite is a very rare mineral form of carbon first discovered in 1967. It is formed when graphite is transformed into a diamond-like structure through shock events, i.e. at high pressure and temperature, but the hexagonal crystal lattice of the graphite is preserved. It is therefore also referred to as hexagonal diamond. These conditions are found in meteoritic impacts, for instance.



# The carbo

atomic number ····· **6** 12,011

density in g/cm³ ····· 2,26 2,50

[He]$2s^2 2p^2$

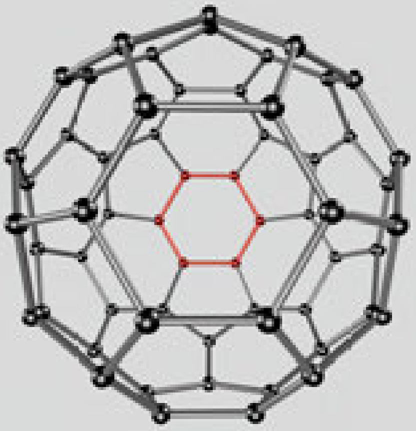
3750 G / 4830

**4, 2, -4**

chemical symbol ····· **C**

chemical name ····· Carbon

### Six faces of a ch
### the allotropic f

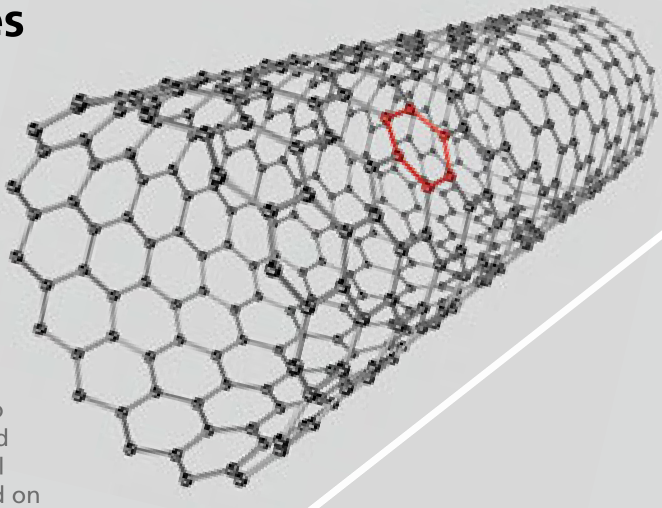


## Fullerenes / buckyballs

The "prototypical" fullerene $C_{60}$ resembles a football. The hollow carbon molecules were first produced in 1985 when researchers shone laser light onto a graphite layer. The most stable form of carbon there is, $C_{60}$ is even found in interstellar space. It consists of 12 pentagons (like all fullerenes) and 20 hexagons, and was named buckminsterfullerene (or buckyball for short) after the architect Richard Buckminster Fuller as it looks like the geodetic domes he constructed.

## Carbon nanotubes

Carbon nanotubes (CNTs) have similar properties to graphene (again: sp$^2$ configuration) and can be pictured as a graphene layer rolled into a cylinder. They are formed in hydrocarbon combustion processes in the presence of a catalyst – or, as Empa recently managed to demonstrate for the first time, specifically from precursor molecules. Although there are countless forms of CNTs, they are generally divided into two rough categories: single-walled and multi-walled CNTs. Their hexagonal lattice structure can also be twisted on its axis, which is referred to as chirality. Depending on the chirality, CNTs are either semiconducting or metallic.



## n cosmos

standard atomic weight
electronegativity
electron configuration
melting point / boiling point in °C
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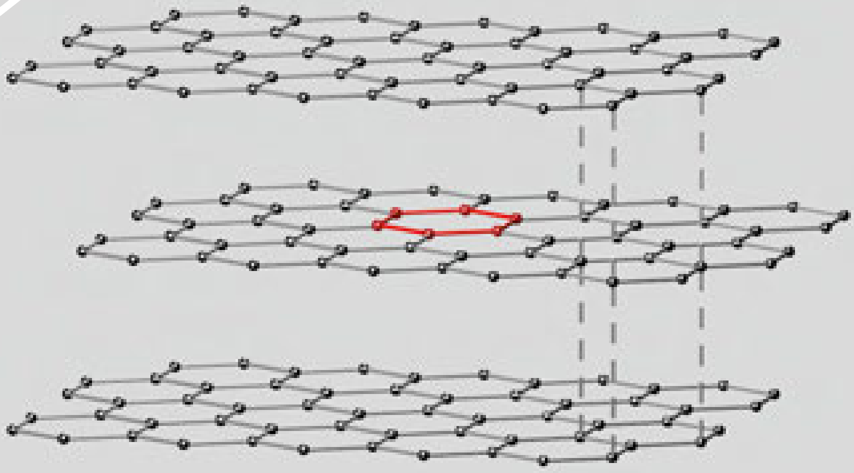
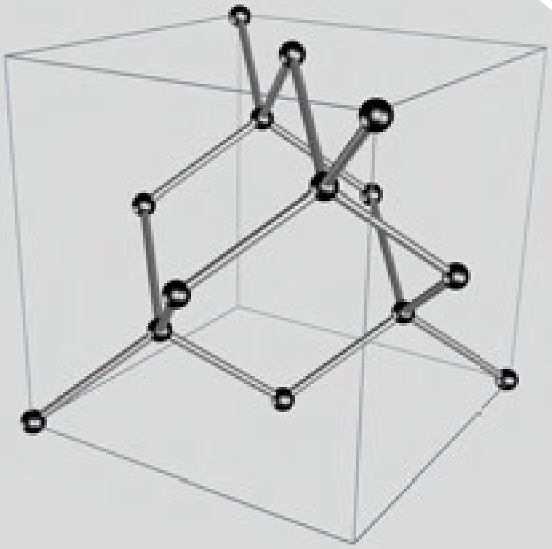
### emical element:
### orms of carbon



## Graphite

Natural graphite consists of countless layers of carbon atoms lying on top of each other, arranged in the form of a hexagonal honeycomb structure. This is referred to as an sp$^2$ configuration. The bond between the layers is very weak, the material is extremely soft, which is why a graphite pencil leaves a grey trace on the paper when the individual flakes are rubbed away: the layers are worn down.



## Diamond

In contrast to many other varieties of carbon, the carbon atoms in diamond are bound to each other tetragonally (i.e. in four spatial directions) and do not have any free electrons. This is referred to as an sp$^3$ configuration. In many respects, diamond is the “opposite” of graphite: it is an electrical insulator, an excellent heat conductor and the hardest natural material.