Chips from a Sheet

Material scientists are pinning their hopes for the electronics of the future on graphene more than almost any other substance. The teams working with **Klaus Müllen**, Director at the **Max Planck Institute for Polymer Research** in Mainz, and Jurgen Smet, group leader at the Max Planck Institute for Solid State Research in Stuttgart, are striving to make these hopes a reality.

TEXT **CHRISTIAN J. MEIER**

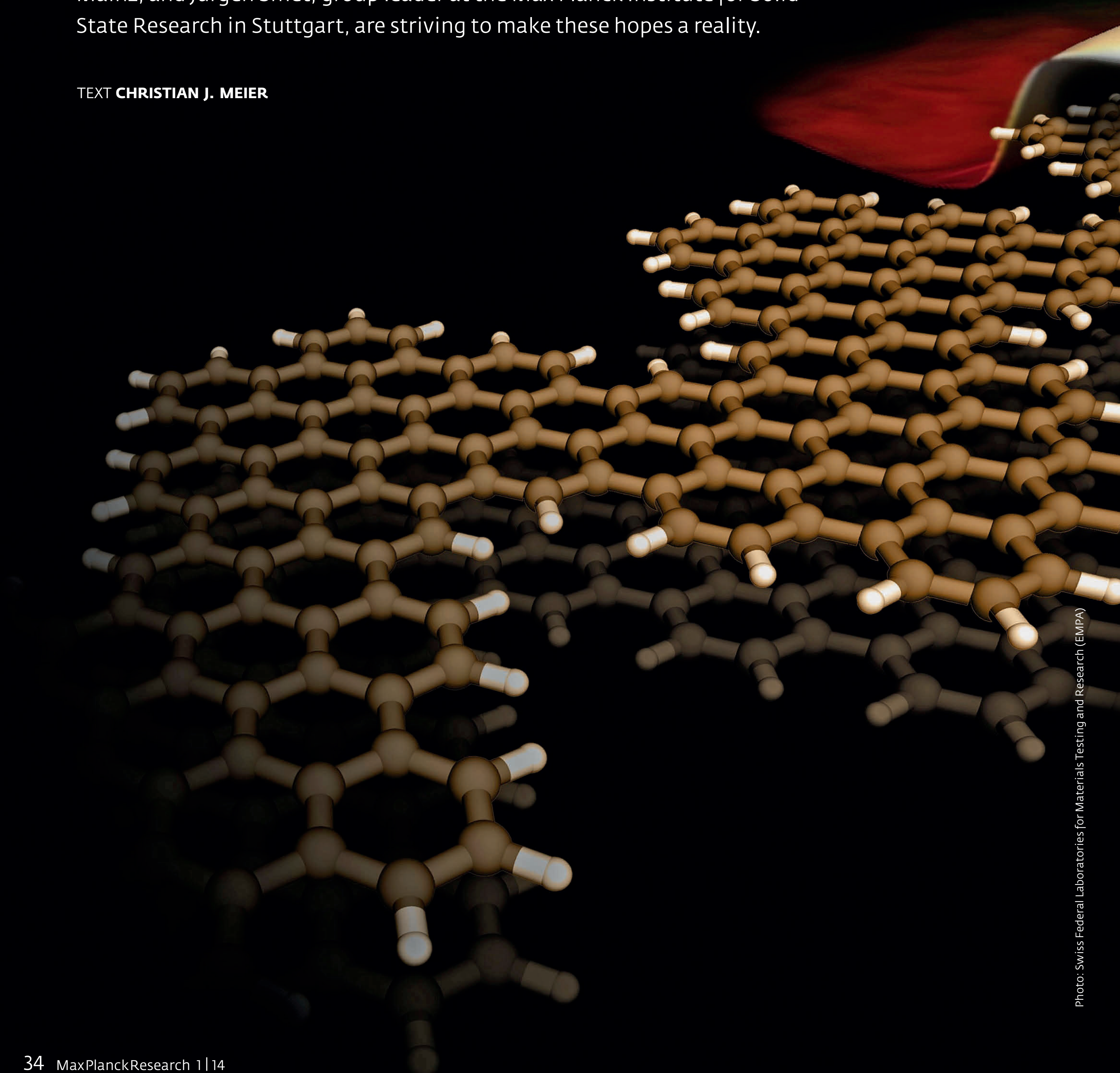
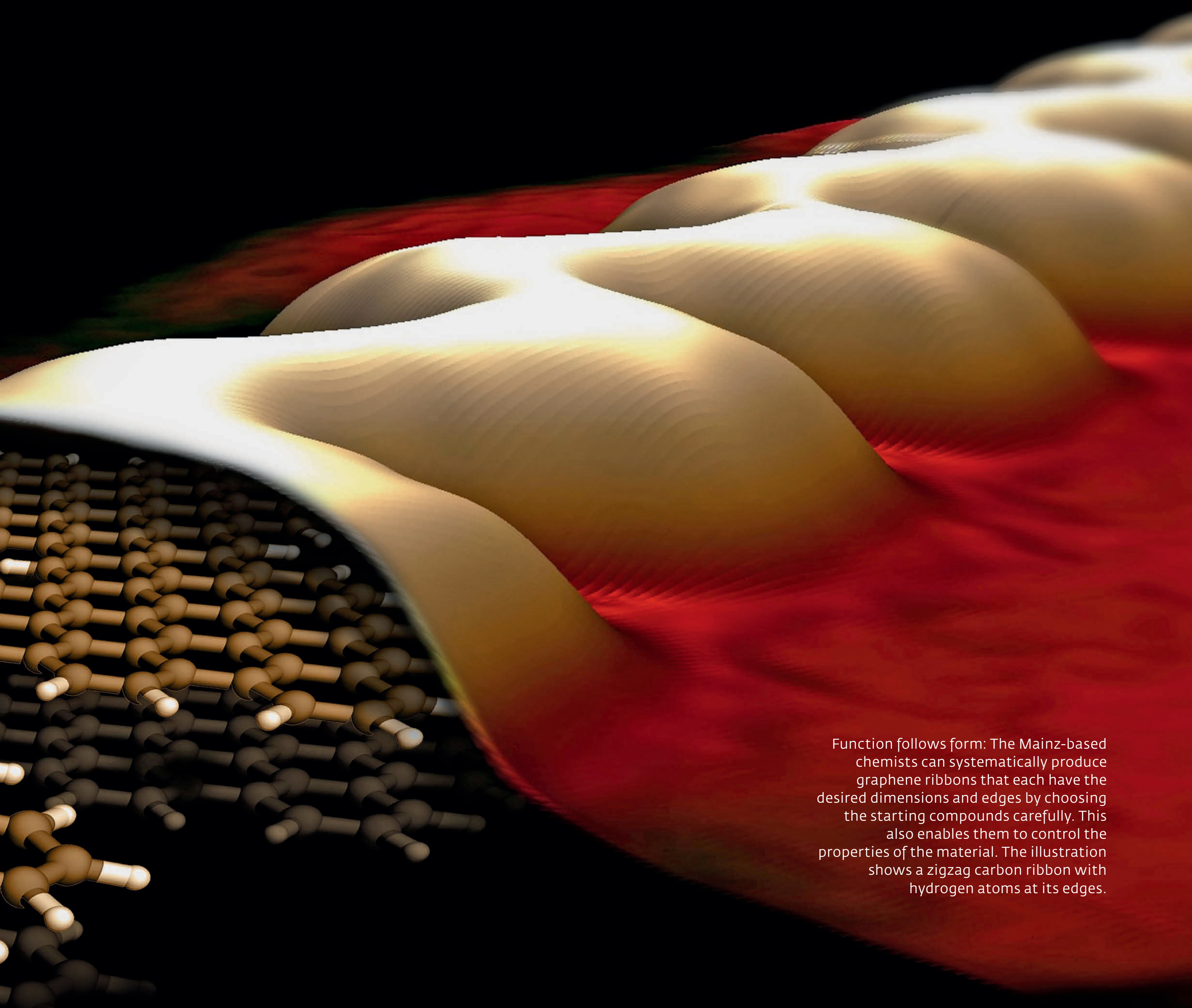


Photo: Swiss Federal Laboratories for Materials Testing and Research (EMPA)



Function follows form: The Mainz-based chemists can systematically produce graphene ribbons that each have the desired dimensions and edges by choosing the starting compounds carefully. This also enables them to control the properties of the material. The illustration shows a zigzag carbon ribbon with hydrogen atoms at its edges.

Compared with modern scientists, Stone Age people had an easy life. Though they had to be skilled at making tools such as hand-axes, axes or arrowheads for various purposes, they found the stone they used for them in their natural environment. Today, in contrast, scientists often have to first develop the material before they can construct devices with different functions. “We need material innovation,” says Klaus Müllen from the Max Planck Institute for Polymer Research in Mainz, whose work is dedicated to the carbon material graphene. It could be argued that Müllen and his team in Mainz found the material of their research dreams long ago – a material that some in the media like to call a miracle material because of its unique mechanical, electrical and thermal properties that promise to provide a whole potpourri of new applications. Not all graphene is the same, however – its properties depend very much on its form, on the other substances it is in contact with, and on the ambient conditions to which it is exposed.

The network of carbon atoms arranged in a honeycomb pattern and having a thickness of just one atomic layer is more a material platform than a material – a playground for researchers, a versatile superhero of a material that develops different strengths depending on its particular manifestation.

The chemist Müllen and his team in Mainz, and the physicist Jurgen Smet at the Max Planck Institute for Solid State Research in Stuttgart, are therefore looking for new forms of carbon sheets for innovative graphene designs that enable functions that the simplest form of graphene – the uniform two-dimensional carbon film – doesn’t.

The researchers are fascinated by the exotic nature of graphene: electrons

The color is determined by the length of the molecules: In solution, dimers of the starting compound from which Akimitsu Narita synthesizes the carbon ribbons appear yellow (right vial) and trimers appear red (center vial). The finished graphene nanoribbons color the solution violet.

move more quickly and collision-free in it than in any other material; it conducts heat better than diamond – long the unsurpassed champion here; and its tensile strength would make it possible for a suspension bridge to span the ocean from Ireland to the Azores – from a purely mathematical point of view, of course. “It is such wonderful physics,” says Jurgen Smet, whose eyes sparkle as he describes one of his research projects on graphene.

Intertwined with their basic research is the prospect of the subsequent industrial mass production of their material innovations, be it for more powerful nanoelectronics, for rechargeable batteries with a longer life and extremely high capacity, or for superconductors that conduct electricity without loss.

The carbon sheets are a natural choice for nanoelectronics applications because electrons race through the material at very high speeds, and because the sheets are extremely thin. Thanks to the nimble charge carriers, electronic components based on graphene could compute faster and thus make it possible to build more powerful computer chips than can be achieved with current silicon technology.

IN NARROW RIBBONS, GRAPHENE BECOMES A SEMICONDUCTOR

Some digital circuit components could also be produced on a significantly smaller scale from the inconceivably thin graphene than from silicon. This would further increase the power of computer chips. In addition, the flat material offers scientists the opportunity to construct three-dimensional digital circuits, allowing several times the computing power to be accommodated on a given chip area.

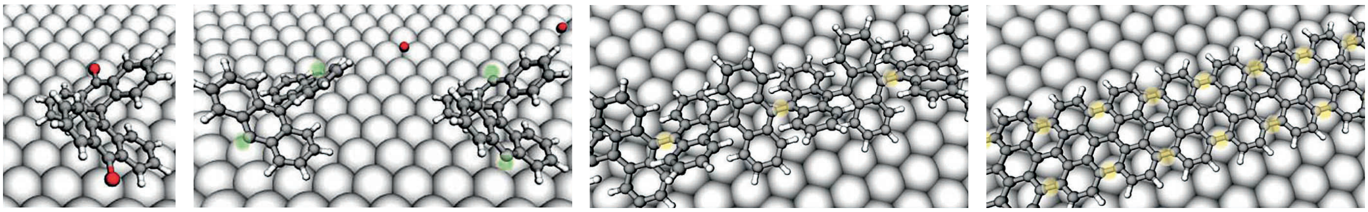
There is a drawback, however: digital circuits require components that can be switched to and fro between two states – “on” and “off” – so-called transistors. This requires semiconductor materials like the silicon used in today’s computer chips. Yet pure, two-dimensional graphene isn’t a semiconductor, but a semimetal.

The two classes of materials differ in their band gap – a semiconductor has one, while a semimetal like graphene does not. The band gap separates the so-called valence band, in which electrons remain immobile, and the conduction band, in which the charge carriers race through a material and can thus contribute to the electrical conductivity.

To overcome the band gap, electrons need a shot of energy. In a semiconductor, the energy difference between the two bands is large enough for the material to be switched from conducting to non-conducting by applying a voltage. It is therefore suitable as a transistor in a digital circuit.

But graphene wouldn’t be graphene if it couldn’t acquire a band gap as a re-

Photo: Thomas Hartmann



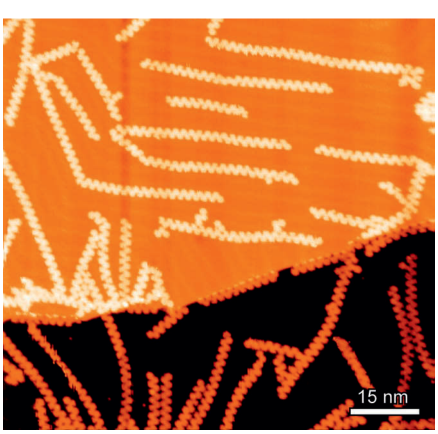
1 2 3 4

Chemistry with connections: The chemists in Mainz use, for example, a bromated bianthryl (1) as their starting material. The bromine atoms (red) separate from the monomers if they are deposited onto a gold or silver surface at a temperature of around 200 degrees Celsius, and radicals are formed – indicated by the green dots (2). These combine at the coupling sites (yellow) to form a polymer in which the individual anthryl units are twisted with respect to each other (3). At 400 degrees Celsius, hydrogen is removed from the polymer, and the anthryl units link up at the yellow dots to form a flat ribbon (4).

sult of a change in its form. A promising and intensively researched approach is provided by tagliatelle-shaped graphene nanoribbons, or GNR for short.

Just why the ribbon, which is only a few nanometers wide – a nanometer being one millionth of a millimeter – has a band gap can be understood by looking at the wave nature of electrons. The width of the graphene ribbon corresponds approximately to the wavelength of the elementary particles. What happens is thus similar to what happens with a violin string: it oscillates at different frequencies depending on its length. Similarly, a GNR of a certain width allows only certain frequencies of electron waves. The distance between two allowed frequencies always corresponds to an energy separation.

The result is that a band gap is generated – an energy range in which the electrons can't exist. The narrower the ribbon, the larger its band gap. Whether there is a band gap at all and how large it is depends also on the form of the ribbon edges.



Graphics: Nature 2010 (top and bottom)

Zigzags of carbon: The image taken by a scanning tunneling microscope shows graphene ribbons on the gold surface on which they were produced.

This complexity, in Müllen's opinion, makes the production of graphene nanoribbons a task for chemists. Why? Physicists produce the ribbons in different ways. They sort of cut out ribbons of graphene with electron beams. Or they slit open carbon nanotubes, practically tubular graphene, and unroll them – just like making tagliatelle from macaroni.

THE FORM OF THE EDGES AFFECTS THE PROPERTIES

"But these methods don't give us any control over what the edges look like," says Müllen. It's very important to be able to produce custom-made edges, because irregular edges slow down the electrons. This means one of graphene's major advantages – the speed of its electrons – is lost. But even when the edges are regular, this shape influences the electronic properties.

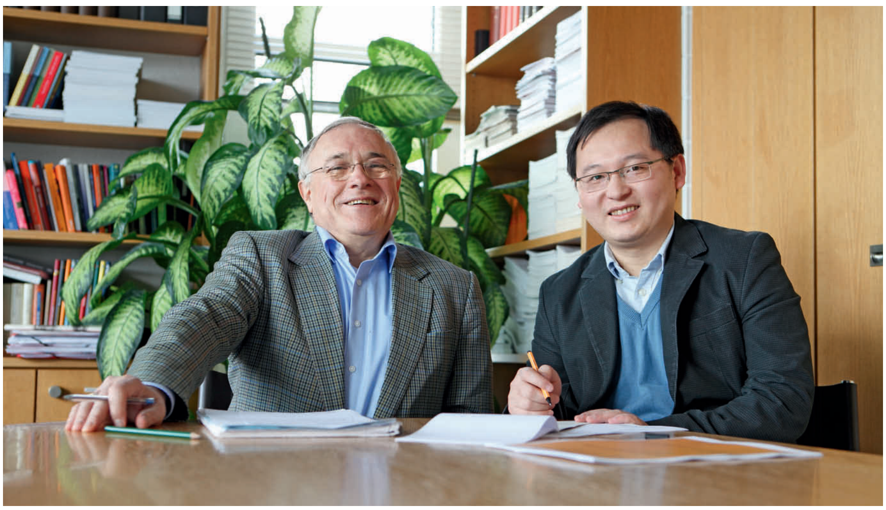
At the edges of the carbon ribbons, the carbon hexagons that make up graphene can, for example, be offset from one another. This produces adjacent bays resembling armchairs at the edge. Or the edge takes the form of a zigzag. The armchair version leads to a band gap, while the zigzag version doesn't necessarily. Instead, the zigzag version has at its edge electrons with a specific spin – a magnetic property that makes the particles resemble the needles in a compass. This makes these types of nanoribbons interesting for a new form of electronics – spintronics – which aims to store and process bits, not with the electronic charge as previously, but with the spin.

The researchers in Mainz can control the form of the ribbons and thus also the form of the edges down to the level of individual atoms. They can guarantee, for example, that the armchair version is formed because they plan where each individual carbon atom will sit in the finished GNR. They achieve this by taking more or less the opposite path of the one the physicists use. Instead of cutting up a large sheet of carbon, they build up the ribbon from smaller hydrocarbon molecules. So they work more like bricklayers, constructing a building according to a plan, brick by brick, rather than like sculptors, removing material from a workpiece with a chisel.

With the bottom-up method, they come very close to the highest art of nanotechnology, the construction of materials atom by atom – just as Eric Drexler, the pioneer of nanotechnology, forecast in the 1980s. Since this method allows the scientists to control the structure of the product as precisely as possible, they can also control its physical and chemical properties right down to the fine details.

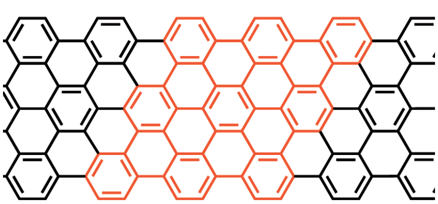
This allows nanoelectronic components to be designed in a specific way, something sculpting methods couldn't do, because even the most delicate chisels the semiconductor industry uses to chisel transistors out of silicon, for example, are too coarse to work on structures down to the level of individual atoms with precision.

In order to build up the carbon nanoribbons using the bottom-up method, the Mainz researchers use molecules

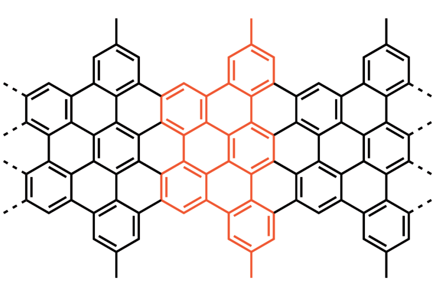


top: Producing custom-made graphene ribbons: Klaus Müllen and Xinliang Feng develop the synthesis paths to produce graphene nanoribbons with a defined length and width, and with the edge form desired in each case.

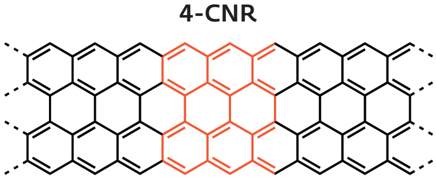
bottom: It's the edge that counts: Graphene ribbons with edges shaped like adjacent armchairs (9-ANR, top) or with small indentations in the edge (4-CNR, center) have a band gap and thus fulfill a condition for electronic semiconductor components. Carbon ribbons with a zigzag edge (4-ZNR, bottom), in contrast, have no band gap.



9-ANR



4-CNR



4-ZNR

composed of several hexagonal hydrocarbon rings. At two of their ends, these monomers bear a different atom, for example bromine instead of a hydrogen atom. When the chemists heat the monomers on a metal surface such as gold to 200 degrees Celsius, the placeholder atoms separate off, leaving behind reactive coupling sites on which the monomers link up to form a chain.

Since the hydrogen atoms at the ends of the chain-linked monomers get in each other's way, the chain is initially wavy. The researchers remove these interfering hydrogen atoms by heating the intermediate product to around 400 degrees Celsius. The benzene rings of neighboring monomers now combine to form a continuous nanoribbon. The Mainz-based researchers have developed a similar method to produce ribbons in solution as well. This is more practical for large-scale technical applications.

Aside from the control over the edges, the method provides some further adjustment options that allow very different carbon nanoribbons to be designed. In the future, these could play very different roles in nanoelectronics. "By choosing the monomers, we can control the ratio of length to width of the GNR," says Müllen's colleague Xinliang Feng.

METHODS SUITABLE FOR MASS PRODUCTION

If the chemists mix in monomers with three placeholders among the molecules with two bromine atoms, Y-shaped ribbons form that can be used in circuits for branching lines. Working in collaboration with researchers at the Swiss Federal Laboratories for Materials Testing and Research in Dübendorf, the scientists in Mainz have even produced GNR linkages with band gaps of different widths. Such heterostructures also play a role in conventional microelectronics and could thus be translated into a new type of nanoelectronics.

Suitably shaped GNRs could also be used in solar cells, because they absorb visible and infrared light, as Müllen's team found out using theoretical computations carried out in collaboration with Belgian and French researchers and BASF.

Müllen's team has been carrying out research with the Ludwigshafen-based chemicals group since 2012 in a joint research lab established especially for the purpose. "What we are doing is basic research, but we are open to application possibilities," says Müllen. This is more than just lip service, given that the production methods developed in Mainz are, in principle, suitable for mass production. For one thing, the monomers are easier to handle as the starting material than graphene. Moreover, both of the chemists' production methods have advantages for industrial manufacturing.

The method of producing the carbon nanoribbons in solution is simple

Photo: Thomas Hartmann; graphic: ACS Nano

Perfectly clean: Wafa Rouabeh, Patrick Herlinger and Jurgen Smet use an oven to deposit carbon onto metal surfaces so that it forms graphene. In order to arrive at meaningful and reproducible results, the researchers investigate the material in the cleanroom. The suits prevent dust particles from detaching from their clothing.

Photo: MPI for Solid State Research – Carmen M. Müller

and low cost. Furthermore, it also offers the possibility to produce electronic circuits using rapid, low-cost printing methods. The other method – depositing graphene on surfaces – needs only relatively low temperatures and is thus compatible with current manufacturing methods in the computer industry.

Metals, however, aren't suitable as graphene substrates in electronics because they would short-circuit the component. This is where physicist Jurgen Smet comes into play. One of his graphene projects aims to develop a transfer process. The Stuttgart-based researchers are using various methods in an attempt to transfer graphene from copper substrates to other surfaces.

Although Smet has a passion for basic research, he also has an eye to the eventual industrial production. "We develop methods where the substrate isn't dissolved, in order to prevent the copper from being lost in the process." The researchers use a stamp, for example, that lifts the graphene from the substrate and deposits it onto a different one. "Here, it's important to apply a specified pressure in a way that is reproducible," emphasizes Smet.

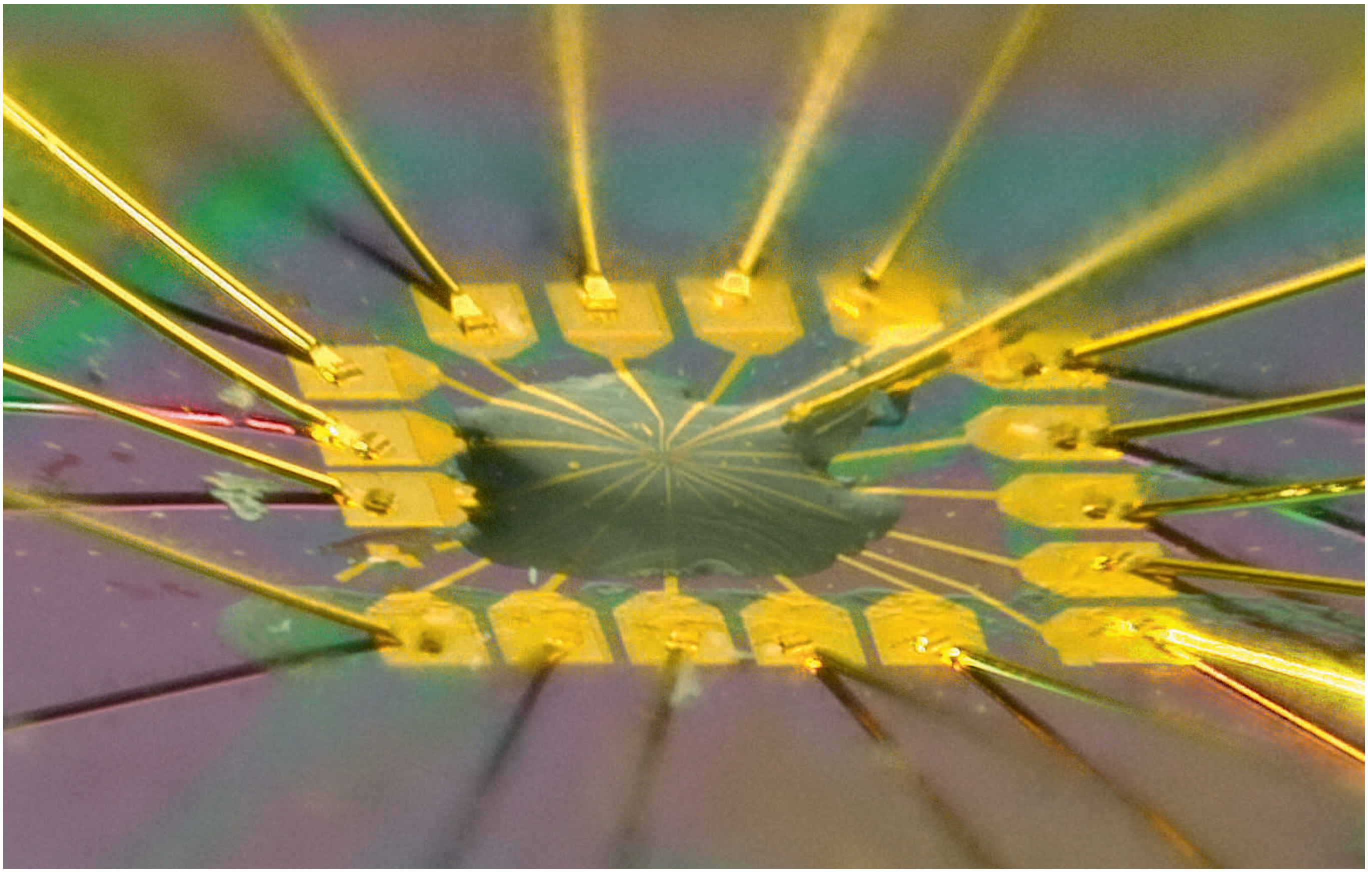
THE MATERIAL IS UNCHARTED TERRITORY

The researcher hopes to achieve this goal in collaboration with the neighboring Fraunhofer Institute for Manufacturing Engineering and Automation. He and his team are trying out different ways to make it possible to use a graphene-coated copper foil as, for instance, the electrode in a galvanic cell. For this, they have versions in which the copper is decomposed only slightly or not at all.

Apart from searching for practical transfer methods, Smet is also working on much more fundamental aspects of graphene. He views the material as uncharted territory that holds many surprises in store. "It combines an unusual number of superlatives," he says, explaining the fascination that graphene triggers in researchers, resulting in a veritable army of scientists around the world investigating the material. The hype has the disadvantage that "the low-hanging fruits have long since been harvested," as Smet puts it. Research is thus delving into more and more detail.

Jurgen Smet would like to make inroads into the uncharted territory of graphene research, as it were, and discover new properties of the material in the process. To this end, he puts flat graphene in different environments, combining it into double layers, for example, wetting it with thin liquid layers, or embedding it between other materials. Applications lie in store here that could be important above and beyond computer electronics – for instance in energy storage or superconductivity, which promises loss-free transmission of electricity.

At the root of all this is the physicist's curiosity. "Graphene is ideal for investigating the interaction between the electrons in it," says Smet. Phenom-



Test bench for a nanomaterial: The researchers in Stuttgart bond graphene samples with particularly conductive gold wires in order to analyze their electronic properties. Here, they dripped an ionic solution onto the material. The ions generate a high charge carrier density in the graphene, as is required, for example, for efficient energy storage devices.

ena such as superconductivity, for example, or so-called Bose-Einstein condensates, are based on such interactions. Physicists around the globe study these macroscopic quantum objects in order to explore what the exotic states of matter have to offer.

The first step in these investigations is to bring large numbers of additional electrons into the graphene so that they interact with each other. “We want to find out how much the electron density in the graphene can be increased,” says Jurgen Smet. There is a possibility that this can be done to such an extent that graphene becomes a material that can be converted into a superconductor at the push of a button.

The physicists produce the starting material for the experiments themselves: sheets of perfect graphene, as large as possible, featuring a perfectly regular honeycomb lattice. In a reactor, they pass methane vapor over a copper foil on which graphene forms in a chemical reaction.

The researchers then dope the carbon sheets with electrons in different ways. One rather simple way to charge the material with electrons involves coating graphene with an electrolyte: a liquid that contains lithium ions. The lithium ions attach themselves to the graphene, so their positive electric charge has to be compensated. Electrons thus migrate from metal contacts into the graphene.

GRAPHENE SUPERCAPACITORS AS ENERGY STORAGE DEVICES

“The separation between the ions and the electrons in the graphene is only one nanometer,” says Smet. The narrow separation between positive and negative charges transforms the graphene wetted with the electrolyte into a capacitor with an extremely high capacity, a supercap. “This means that a very high charge carrier density can be achieved with a small voltage,” explains Smet.

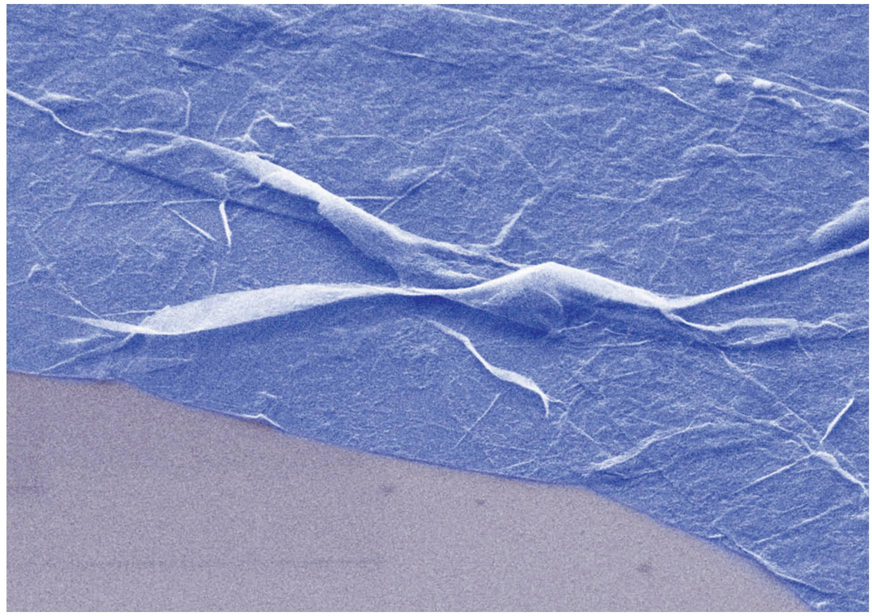
These supercapacitors are interesting not only for the study of interactions between densely packed electrons, but also for applications as energy storage devices. This is because a capacitor can store more energy the denser the charge carriers in it are packed. The Max Planck researchers in Stuttgart are currently trying to develop a production method – one that is also suitable for industrial purposes – for coating the graphene with an electrolyte that is as viscous as possible.

Smet’s team is taking another dip into graphene’s bag of surprises by combining the substance with another two-dimensional material. This material is boron nitride, which forms a flat honeycomb lattice just like graphene, but whose hexagons consist of equal proportions of boron and nitrogen atoms. Unlike graphene, boron nitride is an insulator.

The physicists produce a sandwich by packing two layers of graphene between three layers of boron nitride. This produces two very close but electrically insulated graphene layers. They sort of talk to each other: electrons in one layer interact with atoms in the other layer that are missing an electron – physicists call them holes. Electrons and holes form a species of particle that is new for graphene: excitons, which resemble hydrogen atoms.

Photo: MPI for Solid State Research

Transfer power: For many types of research work, and especially for most applications, graphene must not lie on the electrically conductive metal surface on which it is produced in some methods. The researchers in Stuttgart thus lift it, for example with special stamps, off the metal substrate; here, they subsequently placed it on silicon.



In contrast to electrons and holes as such, excitons belong to the family of quantum mechanical particles known as bosons. These, in turn, can combine in a solid to form a kind of superparticle, a Bose-Einstein condensate. This exotic state of matter normally occurs only at a temperature just above absolute zero, at minus 273 degrees Celsius.

"A hotly disputed theory predicts that, in such a system, a Bose-Einstein condensate could also exist at room temperature," says Smet. Only empirical research could put an end to the controversy, making it a challenge for physicists like him. "The material made of graphene and boron nitride provides us with many options to tweak the properties to achieve this objective," says Jurgen Smet. For example, the density of the excitons can be set to a specific value.

Bose-Einstein condensates at room temperature would be interesting not only for those working in basic research. Some physicists are of the opinion that it would also be possible to use them for quantum computers. This type of computer, which is still very much in its infancy, could solve certain tasks in no time that would take conventional computers an eternity.

Whether as a pure material or a component of new material combinations – the incredibly versatile graphene will likely create quite a stir yet. Max Planck researchers can provide crucial impetus for this. Thanks not least to their skills in constructing new materials at the atomic level, they are teasing more and more new functions out of the simply constructed carbon compounds. "Material innovation," as Klaus Müllen puts it.

So, at some time in the future, we could have the situation where hardly any electronic device will be conceivable without graphene's family of materials. Graphene – as well as other technologically interesting carbon compounds, such as carbon nanotubes and fullerenes, which are shaped like soccer balls – could possibly contribute to a new age, the Carbon Age, where the element might play a similarly indispensable role as stone did in the Stone Age, or silicon in the Silicon Era. ◂

TO THE POINT

- **Graphene consists of a single layer of carbon atoms. The material has unusual mechanical, electronic and thermal properties, making it interesting for many applications, such as electronics.**
- **The structure of graphene can be customized via the chemical starting materials; it is possible, for example, to give its edge a specific desired form, enabling it to be made into a semiconductor.**
- **Various methods, such as stamps, are used to remove graphene from the metal substrate on which it is produced. Only in this way does it become useful for many applications.**
- **Using the individual sheets of carbon, it is possible to investigate strong interactions between electrons, such as superconductivity, when additional charge carriers are pumped into the material.**

GLOSSARY

Bose-Einstein condensate: Multiple bosons – the second type of quantum particle, besides fermions, into which physicists classify particles – can fuse quantum mechanically to form a single particle, usually only at a temperature close to absolute zero, around minus 273 degrees Celsius.

Superconductivity: A material loses its electrical resistance when its electrons combine to form pairs. In all superconductors known to date, this happens at well below zero degrees Celsius – temperatures that aren't very interesting technologically. That is why physicists are attempting to develop superconductors at room temperatures.

Photo: MPI for Solid State Research