Wafer-Thin Electronics

A material can't get any thinner. Graphene consists of just one layer of carbon atoms but that's not the only reason materials scientists are interested in this material: they're fascinated primarily by its extraordinary properties. **ZHI Linjie** and his Partner Group of the **Max Planck Institute for Polymer Research** are using chemistry to optimize graphene for various applications.

TEXT **ALEXANDER STIRN**

Graphene, a gossamer-thin layer of carbon with a structure reminiscent of chicken wire, is the jack of all trades of materials research. It's just one atomic layer thick; in the laboratory, it's 200 times as strong as steel, conducts electricity 100 times better than silicon, is as flexible as plastic, and in individual layers, it's almost as transparent as glass. Physicists and materials scientists are excited. But scientists from other disciplines are showing little interest.

Quite wrong, believes ZHI Linjie: "So far, scientific research has almost exclusively concentrated on the physical properties of graphene, but its chemical behavior is at least as exciting," says the chemist. ZHI, who, at the National Center for Nanoscience and Technology in Beijing, heads the Carbon-rich Nanomaterials Partner Group of the Max Planck Institute for Polymer Research in Mainz, is using the material's chemistry to optimize its properties for specific applications.

In his lab on the eighth floor of the National Center for Nanoscience and Technology in Beijing, there are countless vials holding what at first glance look to be nondescript contents. The containers are neatly labeled – in a mixture of numbers and Chinese characters. Their contents are mainly deep black, but sometimes also rust brown because, in large numbers, the graphene sheets absorb a lot of light. Most of the vials contain a powder; a few, however, hold a thick, dark liquid.

AN INTERESTING BUILDING BLOCK FOR NEW APPLICATIONS

All of the substances, though, are graphene particles in different forms and compositions. They are intended for use as starting products for chemical reactions to create higher performance batteries, more flexible touchscreens and more efficient catalysts. "Fundamentally, graphene is nothing more than an extremely interesting building block for new applications," says ZHI.

His interest in the wonder material, the first experimental production of which was awarded a Nobel Prize in 2010, goes back a long way: After gaining his doctorate in coal chemistry, ZHI worked for five years in Klaus Müllen's Synthetic Chemistry Group at the Max Planck Institute for Polymer Research where he came to know and love graphene. "After a few years, we worked out that, by using the correct strategy, graphene building blocks can be used to produce highly promising materials with unique properties,"says the chemist.

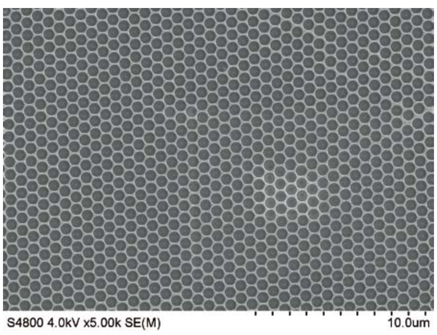
When ZHI returned to China in 2008 and set up his own working group, this knowledge was not all that he took back with him – he had his contacts in Germany, too. "It simply made sense to put Professor Müllen's experience in synthesis together with Professor ZHI's materials expertise in a Partner Group," says Manfred Wagner, who coordinates Sino-German activities in Mainz.

The graphene platelets used in ZHI's laboratory as a material for all kinds of applications consist of just a few hundred, sometimes also a few thousand, carbon atoms. By themselves, however, the two-dimensional molecules, which can be up to ten nanometers in size, show little interest in combining with one another. They're like Lego bricks without the knobs. >

Photo: MPS/Patrick Wack

Promising prospects: ZHI Linjie and his Max Planck Partner Group at the National Center for Nanoscience and Technology explore the chemical behavior of graphene in order to shape the material for new applications.

Chemistry precedes application: ZHI Linjie and his team (above) functionalize graphene and its derivatives chemically before they test the materials in batteries or as electrodes in touchscreens. For a nanolithography technique, which they use, among other methods, to prepare their samples, they use nanomeshes of gold (below).



But it's a different story once the graphene has been chemically treated. One highly promising approach that the chemists in Klaus Müllen's team have already been investigating for some time involves incorporating other atoms or groups of atoms at precisely defined locations in the graphene structure: nitrogen, oxygen or a hydroxyl group consisting of oxygen and hydrogen have different levels of chemical activity and also behave differently than carbon. If they are placed in the correct location, the reaction potential of the graphene block is modified at that point, resulting in the formation of virtual knobs. Larger structures can now be assembled.

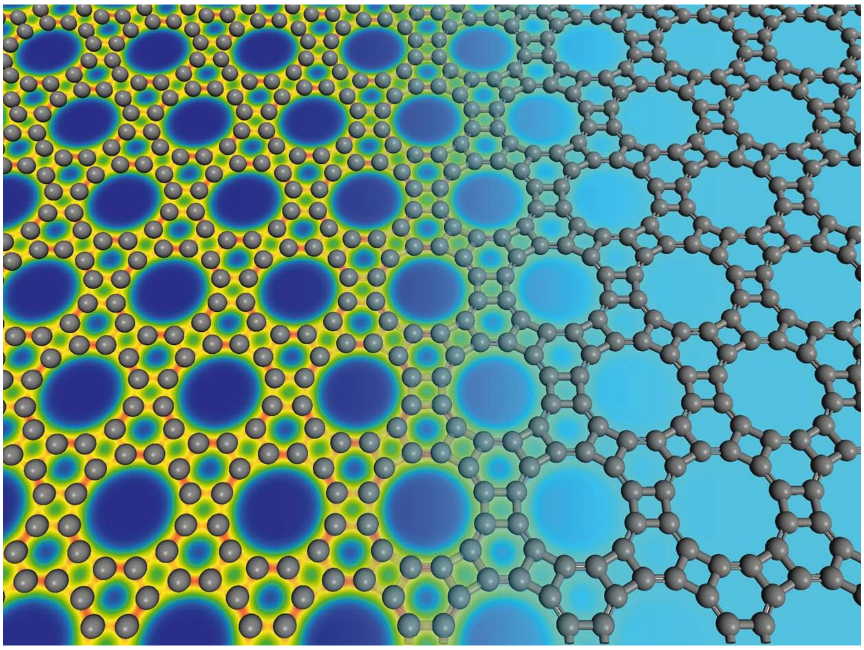
TUNNELS WITH ORDERED GRAPHENE LAYERS FOR BATTERIES

The only snag is getting the chemically active groups or atoms into the correct position. "The right reaction conditions are absolutely vital," says ZHI Linjie. Temperature, pressure, pH, the composition of the solution or the atmosphere in which the reaction takes place, determine the ultimate result. "Chemical bonds often form under precisely defined conditions, which means that we can select the exact position of our molecules," says ZHI.

The conditions also have to be right for the next step: chemical assembly of the manipulated graphene. If the conditions are right, structures with surprising properties can ultimately be obtained – for example, for novel batteries. In today's lithium-ion batteries, the anode (this is the technical term for the electrode that accepts negatively charged particles) is made of graphite, a form of carbon that basically consists of thousands of layers of graphene. "However, these layers are too stretched out for efficient applications," says ZHI. Ions can't readily penetrate, and charging and discharging the batteries takes a very long time.

The situation is different for the graphene platelets produced in Beijing: they are large enough to conduct electricity well, but not so large that the ions can no longer gain easy access to the material. In order to build better batteries, ZHI and his team are placing the chemically modified building blocks in a kind of tunnel that is only a few nanometers in size. In the tunnel, columns of per-

Photos: MPS/Patrick Wack (above), National Center for Nanoscience and Technology, Beijing



Beyond graphene: The theoretically developed structure model of graphenylene. This model demonstrates a unique two-dimensional carbon network with nondelocalized cyclohexatriene.

fectly ordered graphene layers form that can, in turn, be processed to form a porous electrode. Since the columns are extremely thin, the negatively charged battery ions can readily release their charge.

GRAPHENE AS CONTACTS IN TOUCH-SENSITIVE SCREENS

"While it can take eight to ten hours to charge an electric car today, with our batteries it would take only one hour," says ZHI. What this new technique can really achieve is currently being investigated in the laboratory next door, where dozens of self-fabricated batteries, looking like button cells wrapped in plastic film, are hanging from measuring instruments and running through test cycles. The initial results sound encouraging.

Another room accommodates the other major experiment the Partner Group is currently working on: flexible touchscreens with graphene electrodes. Today's smartphones mainly use electrical contacts of indium-tin oxide in their touch-sensitive screens, which is a brittle material whose price has risen meteorically in recent years due to dwindling supplies of indium.

Graphene, which is simultaneously conductive, transparent and flexible, has already long been considered a highly promising alternative. What has been lacking so far, though, is a production process that is capable of producing the films at low cost, in high quality and on a large scale. In the currently preferred method, chemical vapor deposition (CVD), carbon atoms are deposited, for example, on a metallic surface, where they form a thin graphene film. However, this then has to be transferred onto a support film, which is costly and often impairs quality.

On the eighth floor of the National Center for Nanoscience and Technology, ZHI and his colleagues are betting on chemistry being the answer: the Beijing-based researchers take graphite, convert it into graphene oxide, produce a thin film of it on a polyethylene film, and then drive the oxygen out of the graphene oxide in a chemical reaction known as reduction. However, the resultant films are often of poor quality with lots of defects.

A small production line in ZHI Linjie's laboratory shows that things can turn out differently. At the start of the line, there is the neatly rolled, untreated film. At the end are installations for treating the finished product. The actual reaction takes place in the middle, in a nondescript brown box, which is also where the most work is necessary: "Basically, it's a matter of finding the correct selection process," says ZHI Linjie. "We need reliable building blocks that are as large as possible, work as well as possible, and have the fewest possible defects."

After three years as a Partner Group of the Max Planck Institute for Polymer Research, the results have now become "extremely promising," says ZHI. The graphene films produced by the small production line have acceptable quality, transparency and conductivity. Above all, however, they are distinctly cheaper than competing products obtained by vapor deposition.

This has attracted industrial interest. Initial negotiations with companies wishing to make use of the new technology on a commercial scale are already under way. ◂

The Partner Group of Klaus Müllen and ZHI Linjie is conducting research at the National Center for Nanoscience and Technology. It was evaluated in September 2013 and has been extended until April 2015. Partner Group scientists regularly spend time at the Max Planck Institute for Polymer Research in Mainz.

Photo: National Center for Nanoscience and Technology, Beijing