A riot of color in the laboratory: among other projects, Lars Grunenberg, Bettina Lotsch and Julia Kröger (from left) are investigating the wavelengths of light at which their photocatalysts produce hydrogen from water. Here, Lars Grunenberg takes a sample to determine the gas content.

THE LIGHT CONVERTERS

TEXT: KARL HÜBNER

The sun sends more energy to Earth than humanity needs. Researchers led by Bettina Lotsch, Director at the Max Planck Institute for Solid State Research in Stuttgart, are working on materials that can help us put this abundant supply to use for a whole host of purposes – even beyond the energy revolution.

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Every photovoltaic cell shows that sunlight can be converted into an electric current. But, anyone who intends to store this solar power for later use first has to charge a separate battery, and this battery is generally based on lead or lithium-ion technology. The reason behind this separation is that, until now, the production and storage of solar power has relied on completely different materials and components. Against that backdrop, a group of scientists at the Max Planck Institute for Solid State Research caused a minor sensation in 2018 when they revealed a material that could do both at the same time: convert sunlight into electrical energy – and then directly store this energy. As the headline on the Institute's website said at the time, the researchers had created a "solar cell and battery combined."

The material responsible for this breakthrough is called poly(heptazine imide) (PHI) and belongs to the class of materials known as carbon nitrides. Akin to polymers, these molecules feature a strict alternation of carbon and nitrogen atoms arranged into recurring patterns. Although the molecular layers themselves are two-dimensional, they are stacked on top of each other – layer by layer – in a structure resembling "holey" graphite.

Bettina Lotsch has been investigating this group of materials for a long time. The chemist is now the Director of the Nanochemistry Department at the Max Planck Institute for Solid State Research in Stuttgart and an honorary professor at LMU Munich and the University of Stuttgart. "We create functional materials and teach them new tricks, especially with regard to their energy conversion and storage," explains Lotsch. "Some of them are indeed all-rounders." One such group of materials are carbon nitrides, which are so appealing to researchers because they are not only highly stable, but also simple, sustainable and inexpensive to produce.

Initially, the group did not intent to develop a solar battery material. The discovery was a "by-product," so to speak, of research into another property of carbon nitrides – namely, their ability to do photocatalysis. This term is used by chemists to describe the process where a substance absorbs (sun) light and uses this energy to drive a chemical reaction. Photocatalysis is one of the research foci in Bettina Lotsch's Department, where the production of clean hydrogen from water is one of the key reactions →

in the team's experimental work. This reaction also serves as a model for other interesting applications of photocatalysis, such as the synthesis of important basic chemicals by the reduction of carbon dioxide or atmospheric nitrogen. However, hydrogen is also of interest because it is considered to be not only a clean fuel and hence, energy storage medium, but also an environmentally friendly raw material for the future. Indeed, there is a good reason why the German federal government adopted a "National Hydrogen Strategy" in June 2020, in which hydrogen is described as a "key component of the energy transition." At present, however, there is a lack of widespread infrastructure for handling this flammable gas. Moreover, most hydrogen is still produced from natural gas and is therefore not only a fossil energy source, but also – for technical reasons – insufficiently clean for its use in applications such as fuel cells. Although hydrogen could also be obtained electrolytically from water using renewable electricity, the more economically viable – and more elegant – solution would be to split water directly into its components using sunlight. In other words, by using photocatalysis.

Electrons transfer energy to water

In principle, this process was already demonstrated almost 50 years ago, by using titanium dioxide as a photocatalyst – but this approach never became widely used in industry. Modern research focuses on more promising material candidates, including carbon nitrides, which can now be observed in action at a laboratory in Stuttgart. At the bottom of a brightly illuminated glass apparatus, a yellow-colored powder is visible, immersed in a liquid. "The powder is a carbon nitride, the liquid is water, and the reason why the whole thing is so bright is that we're illuminating it from above with a solar simulator," explains Filip Podjaski, a physicist in Bettina Lotsch's research group.

Podjaski explains the underlying principle: "The light excites certain electrons in the material, which in turn

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SUMMARY

Photocatalysts such as poly(heptazine imide) (PHI) or suitable covalent organic frameworks (COFs) use energy contained in (sun) light to drive chemical reactions and, for example, produce hydrogen from water.

PHI can store energy harvested from light and make it available at later times, either for a chemical reaction or in the form of electricity.

This property could be used to create a solar battery that is charged directly by light, to produce hydrogen or other substances, or to power microswimmers.

Testing nanomaterials: the Max Planck team in Stuttgart uses a specially developed reactor to analyze how efficiently photocatalysts can produce hydrogen. The gas produced at the catalyst-coated electrode (light blue) is not visible. The bubbles seen here stem from the noble gas argon, that is used by the researchers to remove oxygen from the reaction solution, which otherwise would distort the measurement.

transfer their energy to the water and thereby produce hydrogen from it." But the exact processes involved are not that simple. On the one hand, the absorbed light must be sufficiently energetic to excite an electron that can drive this reaction. On the other, the photogenerated electrons must be extracted from the material before they return to their ground state and lose their energy. To prevent this, the researchers in Stuttgart add compounds that provide electrons readily to the photocatalyst – "electron donors" – so that the ground state becomes populated again, and the excited electrons remain available for use. Besides, there is also the "co-catalyst," which plays a crucial role in hydrogen production by acting as a matchmaker between the reaction partners. To facilitate most experimental purposes, the researchers currently use the common – albeit rare and expensive – metal platinum as their catalyst. However, they are also working on possible alternatives with a view towards developing a more economical and sustainable solution for future applications.

In principle, such hydrogen production already works well at the laboratory scale, but there are a number of technical issues to be resolved before a process of this kind is ready for widespread use, including in commercially available systems. However, as an aside to their research, the team also asked themselves: what would happen if we simply left out the co-catalyst? Theoretically, with continued exposure to light, more and more electrons would become excited but would have nowhere to go. "Usually, the electrons then decay to their ground state while releasing – or emitting – their energy without practical use, and heat is created," says Filip Podjaski.

However, that was not the case with one particular material, namely with PHI. Provided that an electron donor was present, the photoexcited electrons retained their energy permanently and accumulated within the material, even over the course of several days. In fact, the electrons remained in this state until the scientists added the co-catalyst, which triggered the hydrogen production to begin immediately. This phenomenon was an exciting – indeed an "electrifying" – discovery for the researchers. All of a sudden, they seemed to be able to decouple light absorption and catalysis for a long period of time – just as nature does with the light and dark reactions in photosynthesis, during which light energy is absorbed first and sugar is then produced in a subsequent process. So now, energy could actually be stored temporarily, like in a battery, and then be used for a chemical reaction at the touch of a button and at any point in time – even at night. In the scientific community, the paradoxical term "dark photocatalysis" began making the rounds. And so, the idea of the solar battery was born.

Hydrogen propulsion without a tank

Since then, the scientists have been working on understanding the underlying charging and storage mechanism. After all, how can it be possible for so many negatively charged electrons to accumulate in such a small space? The researchers have since learned that positively charged ions from the material itself and from the surrounding aqueous electrolyte play a stabilizing role.

A material that can store light energy electrically would be useful in a variety of applications. For example, Filip Podjaski envisages hydrogen engines that could work without a fuel tank: "You could use light to accumulate electrons in PHI at any time and then release them whenever you wanted in order to produce the required hydrogen from water." For Bettina Lotsch, the battery-like behavior raises the possibility of "choosing whether to use the stored energy as electricity as

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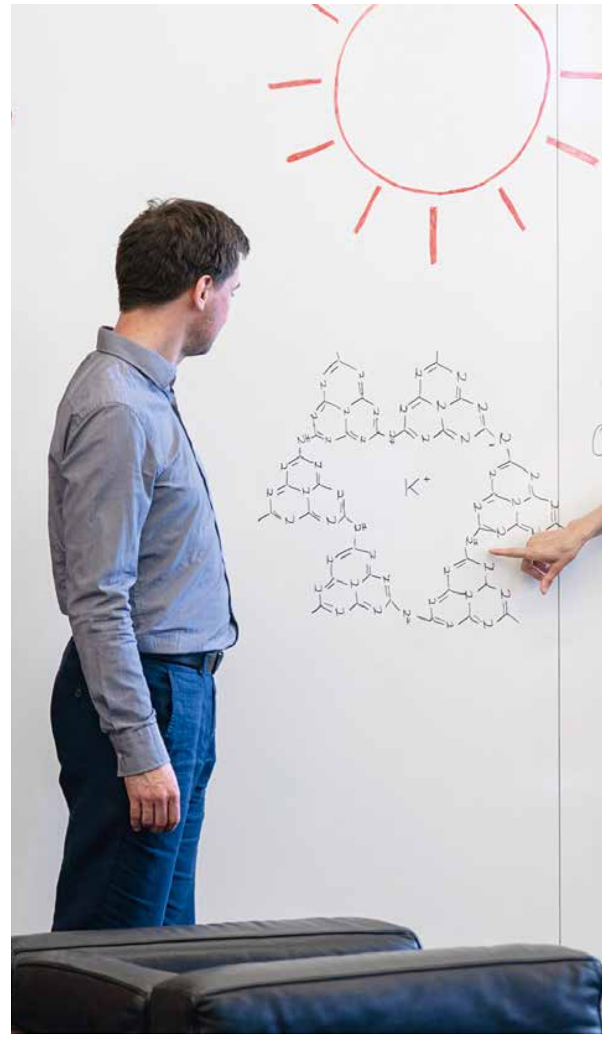

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well." With a simple switch, users could then decide for themselves whether they wanted to use the charged battery to produce hydrogen for a car or to operate a lamp and refrigerator instead. In other words, this technology could provide a versatile solar battery for every household. Moreover, the ability to decouple light absorption from photocatalysis has now proven beneficial for a completely different application – namely, light-driven "microswimmers", which are key topic of research at the neighboring Max Planck Institute for Intelligent Systems (see MaxPlanckResearch 3/2016). It was shown that these swimming micromachines can also be made from PHI particles, while photocatalysis can be used to propel them efficiently through a liquid.

Microswimmers for medicine and environmental protection

Researchers have long known that this type of photocatalytic propulsion system works, but the ability to store the absorbed energy in PHI has now opened up a raft of new applications. "A microswimmer of this kind is not only powered by direct exposure to light, but also continues to move in the dark," says Bettina Lotsch. The chemist even envisages that these microswimmers could one day be designed for use in the human body – once charged, they could continue to swim (in the dark) inside the organism. Another idea is to load microscopic vehicles of this kind with drugs for delivery to a specific location in the body. And perhaps, says Lotsch, a microswimmer made from a photocatalyst could even use catalysis to produce the necessary active agent in situ from substances available in its environment.

However, Lotsch also envisages medical applications of photocatalysis outside of the body. For example, microswimmers could potentially aid the chemical breakdown of metabolic products in the bloodstream during dialysis. Similar applications are conceivable in wastewater treatment – essentially, a photocatalytically active swimmer that would conduct light-powered patrols through dirty water in order to remove unwanted substances. In the future, the researchers led by Bettina Lotsch want to pursue ideas such as these in collaboration with their colleagues at the Max Planck Institute for Intelligent Systems.

But carbon nitrides such as PHI aren't the only materials that the group uses for their photocatalysis research. The scientists also have great expectations for a group of materials known as covalent organic frameworks (COFs). Much like carbon nitrides, COFs form extended layers that then arrange on top of one another. These materials are characterized by their high porosity, with specific surface areas that can reach half the size of a soccer field per gram. This is an ideal characteristic for a photocatalyst, because it is the surface on which reactions catalyzed.

But the key advantage of COFs is that they can, in principle, be constructed from almost any kind of organic building blocks, and these precursor molecules are subject to just a few basic requirements. In other words, they provide huge scope for molecular design. This is particularly beneficial for chemists, in that it allows key properties of a COF to be "tailored" – as Lotsch puts it – by choosing suitable building blocks. In the context of photocatalysis, one key characteristic is light absorption, and the COF designers in Stuttgart have now created novel varieties that absorb from violet to orange – thereby covering almost all of the visible spectrum, which represents about 50 percent of the energy provided by sunlight. On the other hand, if carbon nitrides are used, absorption is limited to blue light only. There is a simple reason why the researchers are mostly interested in materials that absorb light over a broad spectrum: the more light a photocatalyst can absorb from the solar spectrum, the more charge carriers it can supply for catalysis.

Or rather, the more it can potentially supply – because, in order to actually put the absorbed energy to use, it's also important that the electrons retain it for as long as possible and pass it on efficiently. So far, COFs have been unable to rival the effectiveness of the carbon nitrides, but Bettina Lotsch's group is working to change that by subtle variations of the COF building blocks. One day, this may

Searching for the optimum catalyst: Filip Podjaski, Bettina Lotsch, Lars Grunenberg and Julia Kröger (from left) discuss the electronic processes involved in splitting water molecules. An understanding of these processes helps them to develop materials that work more efficiently.

pave the way for something the researchers have high hopes for: the direct, stable storage of solar energy in a completely new type of battery.

Yet the question of sustainability remains unanswered. Indeed, the team in Stuttgart isn't merely looking for functional materials that are particularly effective at tasks such as photocatalysis. "Of course, we also want these substances to be easy and sustainable to produce, ideally from renewable resources," explains Lotsch. Carbon nitrides are absolutely perfect for this, because they can be readily obtained from urea – a natural resource. Depending on the building blocks used, COFs are still ultimately derived from crude oil, but it doesn't stay that way. "As they are organic substances, they are potentially renewable," says Lotsch. In this context, her colleague Filip Podjaski points out that, for historical reasons, the chemical industry can obtain many of its important basic chemicals – and therefore also the derived products, such as the COF building blocks – from a hydrogen/carbon monoxide mixture known as syngas. And although these two components have previously been obtained from fossil sources, they could also be produced from water and carbon dioxide with the help of photocatalysis. Therefore, if suitable recycling concepts were incorporated, these versatile light converters could pave the way for a fundamentally sustainable circular economy, as Podjaski explains. One day, therefore, photocatalysis could potentially turn large parts of chemical production "green".

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GLOSSARY

GROUND STATE
The electronic state of an atom or molecule in which it has a minimum of energy. Electrons can be excited by (visible) light with a suitable energy – that is, light of a suitable color. The so absorbed energy can then be transferred and, hence, released in different ways, while the electrons return to their ground state.

COVALENT ORGANIC FRAMEWORKS
Known as COFs for short, these materials are made from organic building blocks; they have a large specific surface area and are highly variable in terms of their structure and composition, which is due to the variety of potential starting materials.