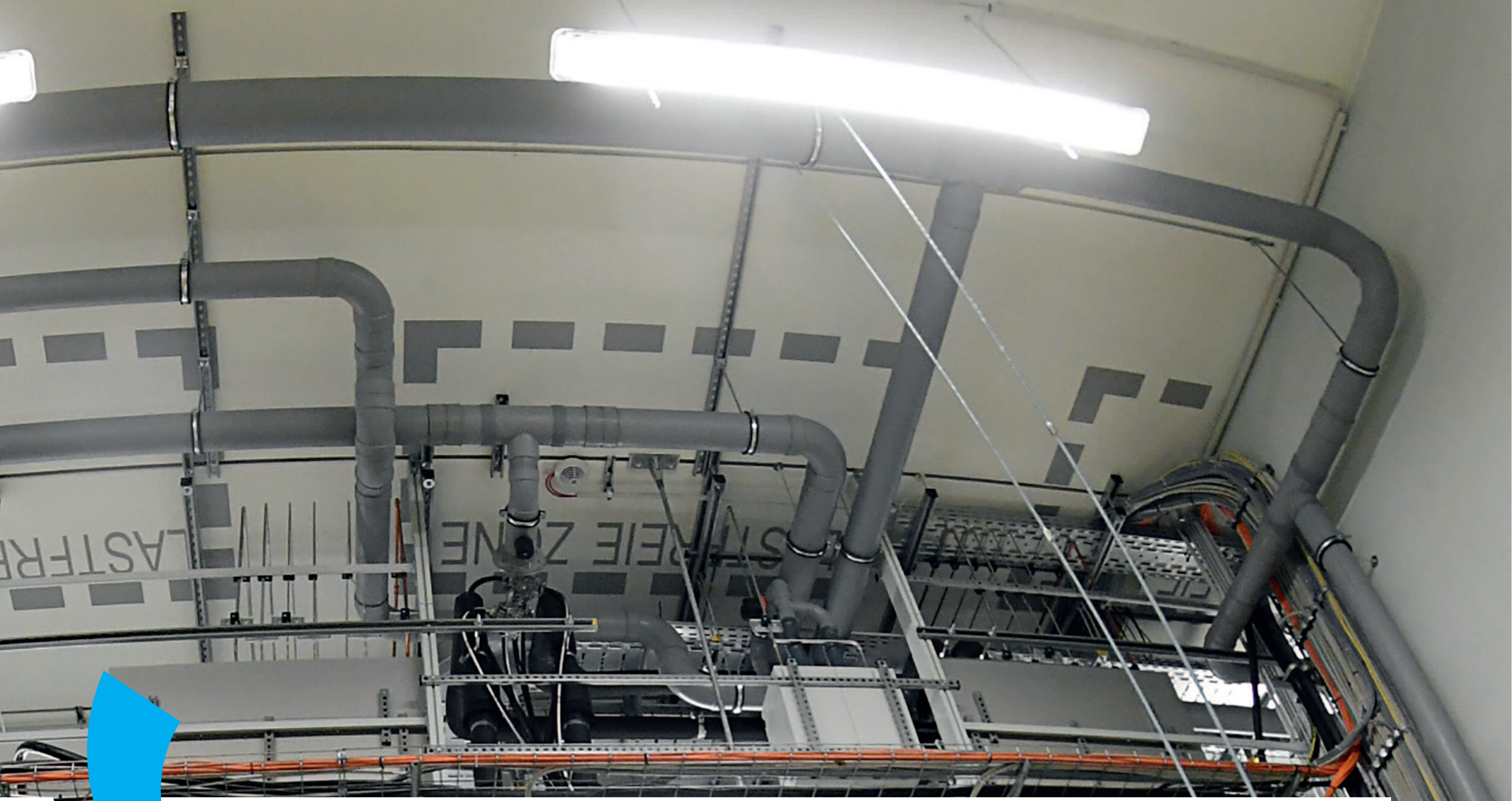
HZB Helmholtz Zentrum Berlin

ENERGY IS OUR MATTER

HIGHLIGHTS 2018

Research highlights at the Helmholtz-Zentrum Berlin für Materialien und Energie



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HZB ANNIVERSARY CELEBRATIONS: REVIEW AND MOTIVATION

Ten years of HZB make for ten years of successful joint research at the two large facilities of Helmholtz-Zentrum Berlin, the synchrotron light source BESSY II and the neutron source BER II. As the newly appointed scientific directors, we, Jan Lüning and Bernd Rech, are both putting in all our efforts to ensure that the HZB's success story continues. In the future, as in the past decades, HZB will continue to upgrade BESSY II and to research new materials and methods that will advance the use of renewable energies.

In awareness of the major challenges that climate change is posing for industrial nations as the main producers of CO_2 emissions, the general public is very interested in our research. We witness this fact every year on the Long Night of Sciences: in 2018 we had 4,700 visitors – more than ever before – come to the Adlershof campus to learn more about our research.

We are working on pioneering solutions, for example, with novel perovskite solar cells, materials for artificial photosynthesis, solar-generated hydrogen, and quantum materials that could reduce the power requirements of computers.

The Long Night of Sciences in 2018 was not only a public attraction for HZB. It also marked the beginning of half a year of anniversary celebrations that continued into 2019. Things to celebrate included HZB's ten years of existence since the fusion of the Hahn-Meitner-Institut (HMI) with the Berliner Elektronenspeicherring-Gesellschaft für Synchrotronstrahlung (BESSY) in 2009 and 20 years of research at BESSY II, which went into operation in 1998.

In the mood-lit BESSY foyer, as part of the celebrations, a delighted audience of employees learned how humorous it can be to look back over one's history in a production of improvisation theatre. Many guests from scientific and political circles followed our invitation to the tipi at the Chancellery, where the celebrations reached a high point.

The anniversary was a great incentive to work towards a successful future for HZB. Together with the HZB employees, we want to set the course for this success. We would already like to thank all of you who are accompanying us on this journey for your support.

The two scientific directors of HZB: Prof. Jan Lüning (left) and Prof. Bernd Rech.

And now, dear readers, we wish you an agreeable and informative read through our HZB Highlight Report 2018.

Prof. Dr. Bernd Rech
Scientific Director

Prof. Dr. Jan Lüning
Scientific Director

STAY UP TO DATE WITH THE HZB NEWSLETTER

Once a month in our newsletter, we keep you informed of the scientific highlights, events, and personnel changes at HZB. Sign up for our newsletter at **www.hz-b.de/newsletter-en**. Subscription is quick and easy and of course protected under the data privacy regulations.

"THE RESEARCH WITH PHOTONS AND ON ENERGY MATERIALS MAKES THE HZB UNIQUE"

In its meeting on 21 November 2018, at the suggestion of the selection committee, the HZB Supervisory Board appointed **Prof. Bernd Rech** and **Prof. Jan Lüning** as the scientific directors of HZB. The move put two internationally recognised experts for photon research and energy research at the top of HZB.

Prof. Lüning, what appealed to you about the new role of scientific director?
JL: HZB has an outstanding reputation in the scientific community. It stands on the two pillars "research with photons" and "research on energy materials", which are an excellent match for each other. That is our greatest strength and it makes HZB unique. It is a very exciting task to continue developing these mainstays, and above all the interface between them, and to make our successes even more visible. For me, the change is also a chance to give something back: while I was a researching scientist, it always benefited me that others were making sure there were excellent research opportunities at the large facilities. Now it is my turn: I see it as my task to continue promoting the research with soft X-rays at HZB and to create the best possible conditions for it.

"The most visible things from the outside are the great successes in energy research. But HZB also enjoys an excellent reputation for BESSY II."

What was your perception of HZB from the outside?
JL: I am a long-standing user at BESSY II, and I know HZB very well. The most visible things from the outside are the great successes in energy research. But HZB also enjoys an excellent international reputation for BESSY II. It is known for its high-resolution spectroscopic methods, which are available for all kinds of materials in solid, gas and liquid form. With the development of "femtoslicing" and "low-alpha mode", the people here have done visionary work. There are also extremely exciting projects in accelerator physics going on at BESSY II, which the community is following with great interest.

"It's about fully exploiting the scientific synergies that energy research and experimentation on the large facilities have to offer."

Prof. Rech, you became the acting scientific director of HZB in May 2016. What made you decide to continue in this capacity?
BR: Just after I was appointed acting scientific director, preparations had to be made for the project-oriented funding evaluation. Although seeing HZB through the POF took a lot of effort, I found I the task very rewarding. It was a fortunate opportunity to learn much more about researching at the large facilities. I also noticed there are many more mutual opportunities than I had realised before. That all motivated me to keep going. It's about fully exploiting the scientific synergies that energy research and experimentation on the large facilities have to offer.

What opportunities do you see?
BR: We have developed a unique profile in the fields of "energy materials", "materials for information technologies" and "research with photons". It was also recognised from the two evaluations that we need to bring these fields even closer together. That's our takeaway, and our common mission. And it is a mission we can accomplish, because there are many points of contact. The soft X-ray synchrotron BESSY II, with its energy and time resolution, offers unique possibilities for researching materials for a climate-friendly

energy supply. That applies as much to materials that convert sunlight into electricity or solar fuels as it does to materials for batteries. New quantum materials promise exciting approaches for energy savings in information technology. The synchrotron helps us better understand the transport of charge carriers, among other things. Conversely, it lends itself to contributing our elaborate synthetic and analytical techniques from energy research to international cooperation projects or making them available to users.

There's a lot being invested currently: BESSY II is being upgraded with new possibilities for time-resolved experiments. What will this upgrade accomplish?
JL: That it will finally be possible to capture rapid processes as "movies" with the synchrotron. The idea is for users to be able to expand their statically gained insights with time resolution. BESSY VSR will deliver short light pulses of 15 and 1.5 picoseconds duration; that way research teams could, for example, characterise the transport of charge carriers on these timescales. Often, researchers don't need anywhere near the ultimate smallest time resolution as you get in experiments with free electron lasers. But synchrotrons offer the highest beam stability and a huge range of experimental methods, which is why there is an interest in offering these short timescales here as well.

"A new synchrotron facility is the only sensible way to meet the needs of the strongly growing user community in Germany."

Why does the user community need a new source for the soft X-ray spectrum in the medium term?
JL: Synchrotrons are currently at the point of a generation change: the fourth generation are diffraction-limited storage rings that produce radiation of a whole new quality. The beams can be focused better onto one point, which allows characterisation of smaller spatial units. It's not just about higher spatial resolution; it also represents a huge step forward for many other experimental techniques. It will grant new insights into quantum materials, for example, or into catalysis and energy research. Plus, every large facility has a natural life cycle, and BESSY II is no exception. We are gradually coming to the phase where BESSY II can no longer offer what is currently technically feasible or what will be in the future. That is why a new facility is the only sensible way to meet the needs of the strongly growing user community. Our task is now to prove just how important BESSY III is for the industrial and technological location of Germany. Our partners and users are giving us a very strong tailwind.


The two scientific directors of HZB: Prof. Jan Lüning (left) and Prof. Bernd Rech.

What role does the location Wannsee play in this?
BR: We are in a transitional phase because the research reactor BER II, which has also received an excellent appraisal, will only continue running until the end of 2019. That is a major challenge. But still, it is important to emphasise the opportunities that reside in this change. Campus Wannsee plays a very important role today in quantum materials and in solar fuels. It offers researchers a wide range of synthetic and analytical methods. HZB has invested a lot into its Wannsee campus in recent years: there are new labs for developing solar fuels and functional oxides, and new laser labs for short-pulse spectroscopy. The campus development is thus part of HZB's overall strategy for a successful future.

Interviewed by Ina Helms and Silvia Zerbe.

IN BRIEF

- "Research with photons" and "research on energy materials" are the two main pillars and strengths that make HZB and its research infrastructure unique.
- Upgrading BESSY II into the variable pulse length storage ring BESSY VSR is an important step towards a next-generation storage ring that will produce radiation of an entirely new quality and will combine the possibilities of time-resolved experimentation.
- The "Energy Materials Research" department is where HZB scientists are working on the next and the next-next generation of solar cells, solar fuels and quantum materials for energy-efficient information technology. This is their contribution to the urgently needed energy transition.

10 YEARS OF HZB, 20 YEARS OF BESSY II

2003

The Nebra Sky Disc

The sky disc discovered in 1999 is from the Bronze Age. The researchers examined it on the BAM beamline of BESSY II and discovered the gold did not originate in Romania, as expected, but in Cornwall, England. From this, conclusions can be drawn about trade routes 4000 years ago.

2009

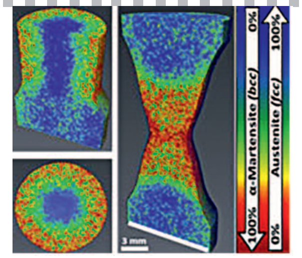
Magnetic monopoles discovered in a magnetic solid

Using neutron scattering, physicists at HZB proved for the first time that magnetic monopoles can arise under very specific conditions. The north and south pole are separated far apart from each other, which normally never happens. The existence of such magnetic monopoles was predicted by quantum physics.

2012

Viking treasure from Oseberg

At BESSY II, Norwegian conservators studied a rapidly disintegrating wooden wagon from a Viking grave near the fjords of Oslo. It had been previously treated with alum, which had since greatly modified the wood fibres. The results are a help in finding new preservation methods for saving such cultural treasures.



2014

What happens to steel under stress?

Stainless steel is expected to withstand extreme loads. To estimate when the material might succumb to fatigue, it is essential to know when and where applied forces will induce changes in the microstructure. Teams at HZB developed a new neutron imaging method for very precisely mapping the crystalline phases and their changes under loads inside the sample.

2009
Founding of Helmholtz Zentrum Berlin für Materialien und Energie (HZB)

2011
Opening of the Competence Centre Thin-Film- and Nanotechnology for Photovoltaics Berlin (PVcomB)

2012
BESSY II is converted to top-up mode to continually inject electron bunches

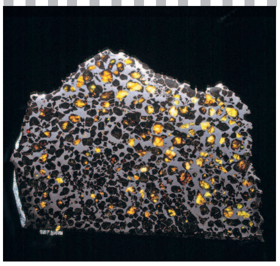
2015
Groundbreaking ceremony for the prototype of an energy recovery linac (bERLinPro)

2016
Inauguration of the energy research laboratory EMIL@BESSY II

2017
3,000th eye tumour patient treated with protons at HZB

2017
Approval of the upgrade BESSY VSR (Variable-pulse-length Storage Ring)

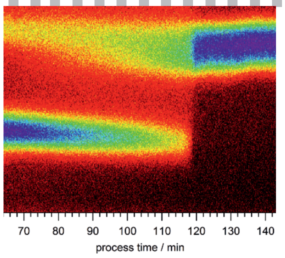
On 1 January 2009, **Helmholtz-Zentrum Berlin für Materialien und Energie** was established. It arose from the fusion of the Hahn-Meitner-Institut and the Berliner Gesellschaft für Synchrotronstrahlung, which had commissioned the **synchrotron source BESSY II** in Adlershof in 1998. For 20 years, cutting-edge research has been conducted at the highest level there, ten years of which was together with the neutron source BER II located in Wannsee, under the roof of HZB. A look back on the highlights from this research.



2015

News from space

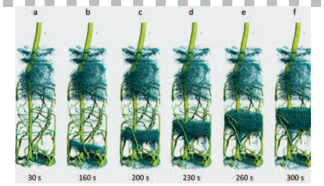
Geologists studied samples of a pallasite meteorite at BESSY II. They identified tiny particles that had aligned themselves magnetically during the early stages of the solar system. The meteorite had thus saved data, so to speak, about our early solar system like a hard drive.



2016

Defects in chalcopyrite solar cells

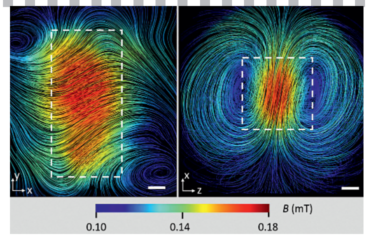
Researchers achieved an important result at BESSY II for optimising thin-film solar cells made of copper, indium, gallium, sulphur and selenium. They observed defects arising during deposition and showed that many defects disappear again on their own during the transition from the copper-poor phase to the copper-rich phase.



2017

Lupine roots observed while drinking

A team from the University of Potsdam observed for the first time in 3D at the Berlin neutron source BER II how lupines draw water through their roots in soil. Together with the HZB imaging group, they improved the temporal resolution of neutron tomography by more than a hundred times for analysing dynamic processes.



2018

Neutrons scan magnetic fields inside samples

With the help of a newly developed method of neutron tomography, an HB team succeeded for the first time in imaging the paths of magnetic field lines inside materials. This "tensorial neutron tomography" promises new insights into superconductors, battery electrodes and other energy materials *(more about this on page 23)*.

Michael Müller
Governing Mayor of Berlin; Senator for Science and Research

"Helmholtz-Zentrum Berlin für Materialien und Energie researches important future topics and ranks among the TOP institutions worldwide. With its highly motivated team in Adlershof and Wannsee, HZB is an indispensable partner in Berlin's scientific landscape and makes a major contribution to our city as a location for cutting-edge research. I congratulate them on their anniversary and wish them much success for the next ten years!"

DEVELOPMENT OF HZB IN THE PAST 10 YEARS

85 ➠ 252
cooperatives in science

64 ➠ 104
PhD students

1 ➠ 9
young investigator groups in research

0 ➠ 3
graduate schools with universities

9 ➠ 30
professors

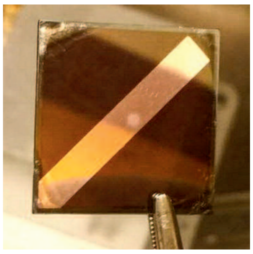
1,064 ➠ 3,750
attendances of School Labs

ENERGY MATERIALS RESEARCH

INSIGHT INTO LOSS PROCESSES IN PEROVSKITE SOLAR CELLS

A team of researchers from the University of Potsdam and HZB were able to find out where the charge carriers in **perovskite solar cells are lost through recombination**. Their results contribute to making targeted improvements to this type of solar cell.

Even solar cells made of a perfect miracle material would never be able to convert 100 per cent of sunlight to electrical energy. This is because the maximum theoretically achievable power is limited by the position of the energy bands of the electrons and by the unavoidable radiation of photons – known as the thermodynamic or Shockley-Queisser limit. Maximum power conversion efficiency for silicon is about 33 per cent, for example. But even this value will never actually be reached. This is due to various kinds of defects causing some of the charge carriers released by sunlight to become lost. In order to approach the maximum value, it is therefore necessary to investigate the various defects in solar cells and to determine which ones lead to losses and how.

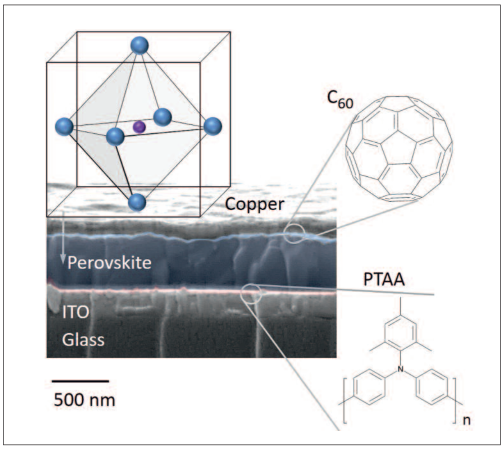


The analysed perovskite cell has a surface area of one square centimetre.

Organometallic perovskite absorber layers are regarded as a particularly exciting new material class for solar cells – in just ten years, their efficiency has increased from three per cent to over twenty per cent, an amazing success story. Now, a team headed by Prof. Dr. Dieter Neher at the University of Potsdam and Dr. Thomas Unold at HZB has succeeded in identifying the decisive loss processes in perovskite solar cells that limit their efficiency. At certain defects in the crystal lattice of the perovskite layer, the charge carriers – electrons and "holes" – that have just been released by sunlight can recombine again and thus be lost. But whether these defects tended to exist within the perovskite layer or instead at the interface between the perovskite layer and the transport layer was unclear until now.

Detailed analyses of losses

To find this out, the scientists employed high-precision photoluminescence techniques of high spatial and temporal resolution. Using laser light, they excited the one-square-centimetre perovskite layer and detected where



With additional layers between the perovskite semiconductor and the hole- and electron-transport layers (red and blue lines), the team at the University of Potsdam was able to further increase efficiency of the perovskite cell.

and when the material emitted light in response to the excitation. "This measurement method at our lab is so precise, we can determine the exact number of photons that have been emitted," explains Unold. And not only that; the energy of the emitted photons was also precisely recorded and analysed using a hyperspectral CCD camera.

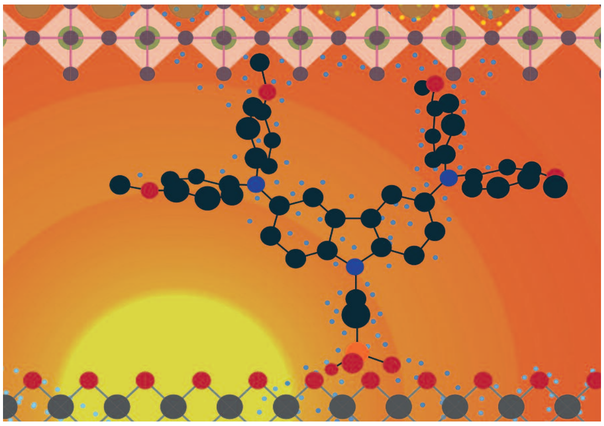
"In this way, we were able to calculate the losses at every point of the cell and thereby determine that the most harmful defects are located at the interfaces between the perovskite absorber layer and the charge transport layers," Unold reports. This is important information for further improving perovskite solar cells, for instance by adding intermediate layers that have a positive effect, or through modified fabrication methods. With the help of these findings, the group led by Dieter Neher and Dr. Martin Stolterfoht at the University of Potsdam has succeeded in reducing interfacial recombination and thus increasing the efficiency of perovskite solar cells of one square centimetre in size to well over 20 per cent. *arö*

Nature Energy, 2018 (DOI: 10.1038/s41560-018-0219-8): Visualisation and suppression of interfacial recombination for high-efficiency large-area pin perovskite solar cells; M. Stolterfoht, C. M. Wolff, J. A. Márquez, S. Zhang, C. J. Hages, D. Rothhardt, S. Albrecht, P, L. Burn, P. Meredith, T. Unold and D. Neher

MOLECULES THAT SELF-ASSEMBLE INTO MONO-LAYERS FOR EFFICIENT PEROVSKITE SOLAR CELLS

A team at HZB has developed a new method for producing **efficient contact layers in perovskite solar cells**. It is based on molecules that organise themselves into a monolayer.

In recent years, solar cells based on metal halide perovskites have achieved an exceptional increase in efficiency. These materials promise cost-effective and flexible solar cells, and can be combined with conventional PV materials such as silicon to form particularly efficient tandem solar cells. An important step towards mass production is the development of efficient electrical contact layers that would allow deposition of perovskite layers onto various substrates. The HZB Young Investigator Group headed by physicist Dr. Steve Albrecht, in collaboration with former DAAD exchange student Artiom Magomedov from Kaunas University of Technology (KTU) in Lithuania, has synthesised a novel molecule that self-assembles into a monolayer (SAM). The team successfully used this new material as a hole-conducting layer in perovskite solar cells. The molecule is carbazole-based and bonds to the oxide of the transparent electrode via a phosphonic acid anchoring group. Due to the anchoring fragment, this molecule organises itself on the electrode surface until a dense, uniform monolayer is formed. The ultra-thin layer exhibits no optical losses and, thanks to its self-organising property, could conformally cover any surface – including textured silicon in tandem solar-cell architectures.



The molecule organises itself on the electrode surface until a dense, uniform monolayer is formed.

Adaptation possible

Extremely low material consumption is achieved with this technique, and the chemical structure of the SAMs can be adapted to the desired application. Thus, SAMs could also serve as a model system for future investigations of the properties of perovskite interfaces and growth. The work took place at the HySPRINT laboratory of the HZB where Albrecht's group is now conducting research on a new generation of self-assembling molecules, which already enable solar cells with efficiencies of more than 21 per cent. Since this approach to perovskite solar cells has never been considered before and can potentially play a role in industrial processes, the HZB and KTU teams have filed a patent application on the molecule and its use. As the scientific interest for this new contact material class is enormous, an issue of the journal “Advanced Energy Materials” featured an illustration from the paper on the front cover.

Amran Al Ashouri

Advanced Energy Materials, 2018 (DOI: 10.1002/aenm.201870139): Self–Assembled Hole Transporting Monolayer for Highly Efficient Perovskite Solar Cells; A. Magomedov, A. Al–Ashouri, E. Kasparavičius, S. Strazdaite, G. Niaura, M. Jošt, T. Malinauskas, S. Albrecht and V. Getautis

NEW RECORDS IN PEROVSKITE/SILICON TANDEM SOLAR CELLS

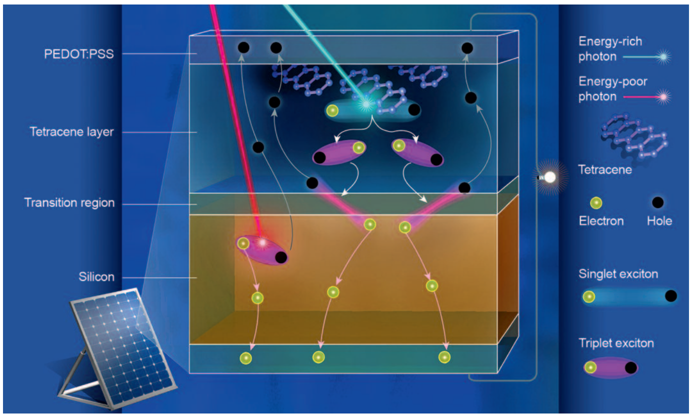
Using microstructured layers, an HZB team has been able to increase the efficiency of perovskite/silicon tandem solar cells, achieving 25.5 per cent, which is the highest published value up to 2018. At the same time, computational simulations were used to investigate light conversion in various device designs with different nanostructured surfaces. This enabled optimisation of light management and detailed energy yield analyses. *arö*

Energy & Environmental Sciences, 2018 (DOI: 10.1039/C8EE02469C): Textured interfaces in monolithic perovskite/silicon tandem solar cells: Advanced light management for improved efficiency and energy yield; M. Jošt et. al.

NEW WAY TO BOOST THE EFFICIENCY OF SILICON SOLAR CELLS

A team from HZB and international colleagues have managed to exceed the **theoretical efficiency limit for silicon solar cells**. They incorporated layers of organic molecules into the solar cells that double the electrical current in a certain energy range.

The principle of a solar cell is simple: for each incident light particle (photon), a pair of charge carriers (exciton) is generated which is split once it reaches the charge-selective electrical contacts. The team led by HZB researcher Prof. Klaus Lips provides a solution to build a solar cell in which certain high-energy photons generate two pairs of charge carriers simultaneously. The effect they exploited is a property of certain organic crystals known as "singlet exciton fission" (SF). For this multiplier effect to be possible, the charge carrier pairs have to fulfil certain quantum physical conditions: all their spins have to be parallel. Such charge carrier pairs are called triplet excitons. These triplet excitons are quite durable and very strongly bound together. The challenge was to split them apart at an interface to silicon. This unbinds the positive and negative charge carriers, permitting them to contribute to the solar cell's current.



Principle of a silicon singlet fission solar cell with incorporated organic crystals.

In a pioneering experiment, the researchers have shown the splitting to be possible. "With implementing this concept successfully, we can make a silicon solar cell with a maximum quantum efficiency of 200 per cent (double the normal limit), and a theoretical efficiency limit of around 40 per cent," says Dr. Rowan MacQueen, an Australian researcher who is realising the charge carrier multiplier solar cell at the HZB.

More of the blue-green light region is used

In their experiment, the HZB researchers integrated a 100-nanometre-thick layer of singlet-fission-capable tetracene crystals into the surface of a silicon solar cell. Using spectroscopic methods, they detected triplet charge carrier pairs in the thin tetracene layer, a signature of singlet fission. "The challenge was to separate the triplet pairs at the silicon interface without significantly disrupting the current flow of the silicon solar cell," Klaus Lips explains. This is because the poorly conducting organic layer bordering on the well-conducting silicon layer could greatly impede the current flow. The splitting is achieved only with the introduction of yet another organic layer of an organic conductor called PEDOT:PSS. "The interfaces play a special role in this structure," says MacQueen, which is why the researchers used X-ray light from the BESSY II synchrotron to study the interface properties. They then fabricated a series of working tetracene-silicon solar cells. A key finding was that the addition of the organic layer did not impede the electrical performance of the silicon cell, which is a critical criterion for producing an efficient device.

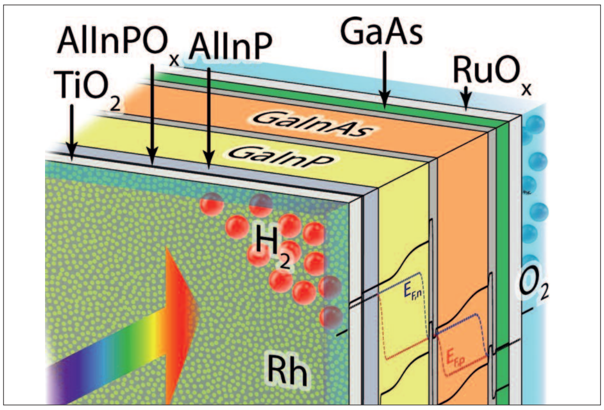
The results show that tetracene absorbs the blue-green portion of light while the silicon absorbs lower-energy photons. From a simulation, the researchers currently estimate that about five to ten per cent of the triplet pairs generated in the tetracene layer could be added to the output power. For Lips, this is a great success: "With this solar cell structure, we have shown that the approach works in principle, and have delivered a workhorse design. And we already know what we have to do to increase the yield of separated triplet excitons to up to 200 per cent". *ih*

Materials Horizon, 2018 (DOI: 10.1039/c8mh00853a): Crystalline silicon solar cells with tetracene interlayers: the path to silicon-singlet fission heterojunction devices; R. W. MacQueen et. al.

WORLD RECORD FOR DIRECT SOLAR WATER-SPLITTING EFFICIENCY

An international team of researchers has succeeded in raising the efficiency of producing hydrogen from direct **solar water splitting to a record 19 per cent at the HZB Institute for Solar Fuels**. They did so by combining a tandem solar cell of III-V semiconductors with a catalyst of rhodium nanoparticles and a crystalline titanium dioxide coating.

Storing sunlight in the form of chemical energy, specifically by using it to produce hydrogen, is a promising path for a sustainable energy supply. This is because hydrogen can be stored easily and used in many ways. If you combine solar cells with catalysts and additional functional layers to form a "monolithic photoelectrode" as a single block, then splitting water becomes especially simple: the photocathode is immersed in an aqueous medium and when light falls on it, hydrogen is formed on the front side and oxygen on the back.



The transparent anti-corrosion layer contains rhodium nanoparticles as a catalyst.

For its monolithic photocathode, the research team from the California Institute of Technology (Caltech), the University of Cambridge and the Technische Universität Ilmenau combined additional functional layers with a highly efficient tandem cell made of III-V semiconductors developed at the Fraunhofer Institute for Solar Energy Systems ISE. This enabled them to reduce the surface reflectivity of the cell, thereby avoiding considerable losses caused by parasitic light absorption and reflection. "This is also where the innovation lies," explains Prof. Hans-Joachim Lewerenz, Caltech, USA, "because we had already achieved an efficiency of over 14 per cent for an earlier cell in 2015, which was a world record at the time. Here we have replaced the anti-corrosion top layer with a crystalline titanium dioxide layer that not only has excellent anti-reflection properties, but to which the catalyst particles also adhere." Prof. Harry Atwater of Caltech adds: "We have also used a new electrochemical process to produce the rhodium nanoparticles that serve to catalyse the water-splitting reaction. These particles are only ten nanometres in diameter and are therefore optically nearly transparent, making them ideally suited for the job."

Stability also improved

Under simulated solar radiation, the scientists achieved an efficiency of 19.3 per cent in dilute aqueous perchloric acid while still reaching 18.5 per cent in an electrolyte with neutral pH. These figures approach the 23 per cent theoretical maximum efficiency that can be achieved with the inherent electronic properties for this combination of layers. "The crystalline titanium-dioxide layer not only protects the actual solar cell from corrosion, but it also improves charge transport thanks to its advantageous electronic properties," says Dr. Matthias May, who carried out part of the efficiency determination experiments at the HZB Institute for Solar Fuels in the forerunner laboratory to the Solar-Fuel Testing Facility of the Helmholtz Energy Materials Foundry (HEMF).

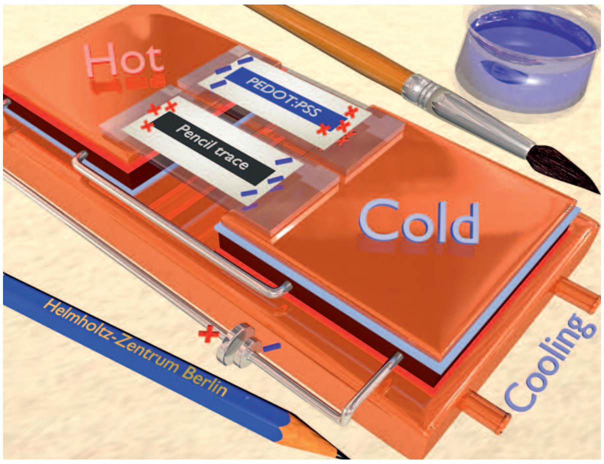
The record figure is based on work that May had already begun as a doctoral student at HZB. "We were able to increase the operating life to almost 100 hours. This is a major advancement compared to previous systems, which would already corrode after 40 hours. Nevertheless, there is still a lot to be done," May explains. Teams at the Fraunhofer ISE and TU Ilmenau are working to design cells that combine III-V semiconductors with lower-priced silicon, which could considerably reduce costs. *arö*

ACS Energy Letters, 2018 (DOI: 10.1021/acsenergylett.8b00920): Monolithic Photoelectrochemical Device for Direct Water Splitting with 19% Efficiency; W.-H. Cheng et. al.

CONVERTING HEAT INTO ELECTRICITY WITH PENCIL AND PAPER

Thermoelectric materials can use **thermal differences to generate electricity**. A team at HZB has demonstrated how this effect can be achieved with simple components in an inexpensive and environmentally friendly way.

The thermoelectric effect is nothing new – it was discovered almost 200 years ago by Thomas J. Seebeck. If two different metals are brought together, then an electrical voltage can develop if one metal is warmer than the other. This effect allows residual heat to be partially converted into electrical energy. Residual heat is a by-product of almost all technological and natural processes, for example in power plants, in every household appliance, and in the human body as well. It is one of the largest under-utilised energy sources in the world – and is still usually completely ignored.



Sketch of the experiment: a normal HB pencil, paper and copolymer varnish are sufficient for a thermoelectric device.

Unfortunately, as useful as the thermoelectric effect is, it is extremely small in ordinary metals. This is because metals have not only high electrical conductivity but also high thermal conductivity, so differences in temperature disappear almost immediately. Thermoelectric materials therefore need to have low thermal conductivity despite their high electrical conductivity. Thermoelectric devices made of inorganic semiconductor materials such as bismuth telluride are already being used today in certain technological applications. However, such material systems are expensive and their use only pays off in specific situations. Another area of investigation is flexible, non-toxic organic materials based on carbon nanostructures, for example, for use in the human body.
A team led by Prof. Norbert Nickel at HZB has now shown that there is a much simpler way to obtain the effect: using a normal HB pencil, they coloured a small area of ordinary photocopy paper in with pencil. As a second material, they applied a transparent, conductive copolymer paint (PEDOT:PSS) onto the surface. It transpired that the pencil traces on the paper deliver a voltage comparable to other, far more expensive nanocomposites that are currently being used in flexible thermoelectric elements. And this voltage could even be increased tenfold by adding indium selenide to the graphite from the pencil.

Poor heat transport explained

The researchers investigated graphite and copolymer coating films using a scanning electron microscope and spectroscopic methods (Raman scattering) at HZB. “The results were very surprising even for us,” explains Nickel. “But we have now found an explanation of why this works so well. The pencil deposit left on the paper forms a surface characterised by unordered graphite flakes, some graphene and clay. While this disorder only slightly reduces the electrical conductivity, heat is conducted much less effectively.”
These simple constituents might be used one day to print thermoelectric components onto paper that are extremely inexpensive, environmentally friendly and non-toxic. Such tiny, flexible components could possibly even be placed directly on the body, where they would use body heat to power small devices or sensors.

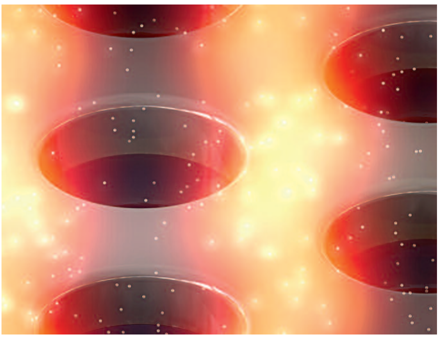
arö

ACS Appl. Mater. Interfaces, 2018 (DOI: 10.1021/acsami.7b17491): Fine Art of Thermoelectricity; V. Brus, M. A. Gluba, J. Rappich, F. Lang, P. Maryanchuk and N. H. Nickel

MACHINE LEARNING HELPS IMPROVE PHOTONIC APPLICATIONS

Photonic nanostructures improve the efficacy of optical sensors for cancer markers or other biomolecules, for example. A team at HZB using computer simulations and machine learning has shown **how the design of such nanostructures can be selectively optimised**.

Nanostructures can increase the sensitivity of optical sensors enormously – provided that the geometry meets certain conditions such as matching the wavelength of the incident light. This is because the electromagnetic field of light can be greatly amplified or reduced by the local nanostructure. The HZB Young Investigator Group "Nano-SIPPE" headed by Prof. Christiane Becker is working to develop these kinds of nanostructures.



The computer simulation shows how the electromagnetic field is distributed in the silicon layer with a hole pattern after excitation by laser. Here, stripes with local field maxima are formed, so that quantum dots shine particularly strongly.

Computer simulations are an important tool for this. Dr. Carlo Barth from the Nano-SIPPE team has now identified the most important patterns of field distribution in a nanostructure using machine learning, and has thereby explained the experimental findings very well for the first time.

Quantum dots on nanostructures

The photonic nanostructures examined in this paper consist of a silicon layer with a regular hole pattern coated with what are known as quantum dots made of lead sulphide. Excited with a laser, the quantum dots close to local field amplifications emit much more light than they do on an unordered surface. This makes it possible to demonstrate empirically how the laser light interacts with the nanostructure.

In order to systematically record what happens when individual parameters of the nanostructure change, Barth calculated the three-dimensional electric field distribution for each parameter set using software developed at the Zuse Institute Berlin. Barth then had these enormous amounts of data analysed by other computer programs based on machine learning. "The computer has searched through the approximately 45,000 data records and grouped them into about ten different patterns," he explains. Finally, Barth and Becker succeeded in identifying three basic patterns among them in which the fields are amplified in various specific areas of the nanoholes.

This allows photonic crystal membranes based on excitation amplification to be optimised for virtually any application. This is because some biomolecules accumulate preferentially along the hole edges, for example, while others prefer the plateaus between the holes, depending on the application. With the correct geometry and the right excitation by light, the maximum electric field amplification can be generated exactly at the attachment sites of the desired molecules. This would increase the sensitivity of optical sensors for cancer markers to the level of individual molecules, for example. arö

Communications Physics, 2018 (DOI: 10.1038/s42005-018-0060-1): Machine learning classification for field distributions of photonic modes; Carlo Barth and Christiane Becker

X-RAY ANALYSIS OF CARBON NANOSTRUCTURES HELPS IN MATERIAL DESIGN

Nanostructures made of carbon are extremely versatile: they can absorb ions in batteries and supercapacitors, store gases and desalinate water. How well they cope with the respective task depends largely on the structural features of the nanopores. A new study from HZB has now shown that structural changes that occur due to morphology transition with increasing temperature of the synthesis can also be measured directly – using small-angle X-ray scattering. *arö*

Carbon, 2019 (DOI: 10.1016/j.carbon.2019.01.076): Carbide Derived Carbons Investigated by Small Angle X-ray Scattering: Inner Surface and Porosity vs. Graphitization; E. Härk, A. Petzold, G. Goerigk, S. Risse, I. Tallo, R. Härmas, E. Lust and M. Ballauff

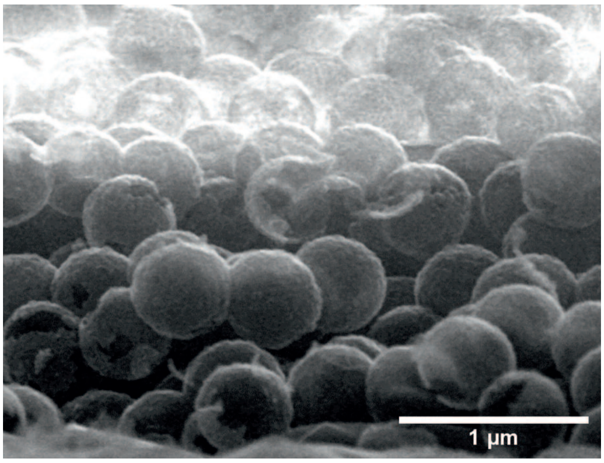
NANODIAMONDS AS LOW-COST PHOTOCATALYSTS

Within the framework of the EU project DIACAT, researchers have doped diamond materials with boron and shown at BESSY II how they could significantly improve the photocatalytic properties. This paves the way for the **production of methanol using water and CO_2**.

Climate change is in full swing and will continue unabated as long as we do not succeed in significantly reducing CO_2 emissions. For this, we will need to use all our options. One idea is to return the greenhouse gas CO_2 into the energy cycle: CO_2 could be processed with water to make methanol, a fuel that can be excellently transported and stored. However, the reaction, which resembles a partial process of photosynthesis, requires energy and catalysts. If we were to use the energy from sunlight this way and succeeded in developing light-active photocatalysts made of inexpensive and abundantly available materials, instead of rare metals like platinum, we would come a good step closer to our goal of climate-neutral production of "green" solar fuels.
A candidate for such photocatalysts are so-called diamond nanomaterials – these are not precious diamonds, but tiny nanocrystals of a few thousand carbon atoms that are soluble in water and look more like black slurry. Another candidate is nanostructured "carbon foams" of high surface area. For these materials to become catalytically active, however, they must be excited by UV light. Only this spectral region of sunlight is rich enough in energy to transport electrons from the material into a "free state". And only then can solvated electrons be emitted in water and react with the dissolved CO_2 to form methanol.

Doping with boron increases the band gap

Unfortunately, the UV component in the solar spectrum is not very large. Photocatalysts that could also use the visible spectrum of sunlight would therefore be ideal. This is where the work of HZB-scientist Tristan Petit and his cooperation partners in DIACAT comes in. Modelling the energy levels in such materials, performed by Karin Larsson in Uppsala University, shows that intermediate stages can be built into the band gap by doping with foreign atoms. Boron, a trivalent element, appears to be particularly important. Petit and his team therefore investigated samples of polycrystalline diamonds, diamond foams and nanodiamonds. These samples had previously been synthesised in the groups of Anke Krüger in Würzburg and Christoph Nebel in Freiburg.



Doping carbon foams with foreign atoms improves their photocatalytic properties, making the material a new hope for the production of methanol.

At BESSY II, X-ray absorption spectroscopy was used to precisely measure the unoccupied energy states into which electrons could possibly be excited by visible light. "The boron atoms present near the surface of these nanodiamonds actually give rise to the desired intermediate stages in the band gap," explains PhD student Sneha Choudhury, first author of the study. These intermediate stages are typically very close to the valence bands and thus do not allow the effective use of visible light. However, the measurements show that this also depends on the structure of the nanomaterials. "We can introduce and possibly control such additional steps in the diamond band gap by specifically modifying the morphology and doping," says Tristan Petit. Doping with phosphorus or nitrogen could also offer new opportunities.

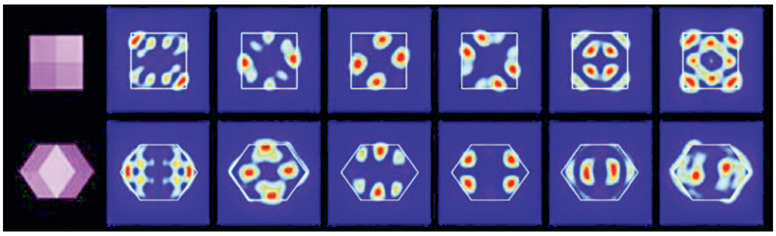
arö

Journal of Materials Chemistry A, 2018 (DOI: 10.1039/c8ta05594g): Combining nanostructuration with boron doping to alter sub-band-gap acceptor states in diamond materials; S. Choudhury, B. Kiendl, J. Ren, F. Gao, P. Knittel, C. Nebel, A. Venerosy, H. Girard, J.-C. Arnault, A. Krueger, K. Larsson and T. Petit

LUMINESCENT NANO-ARCHITECTURES OF GALLIUM ARSENIDE

A team at HZB has succeeded in growing **nanocrystals of gallium arsenide on tiny columns of silicon and germanium**. This enables extremely efficient optoelectronic components for important frequency ranges to be realised on silicon chips.

Gallium arsenide semiconductors have better optoelectronic properties than silicon. Those properties can be controlled and altered by specific nanostructures. Dr. Sebastian Schmitt, Prof. Silke Christiansen and their collaborators have succeeded in creating such a nanostructure on a silicon wafer covered with a thin, surprisingly crystalline layer of germanium. Colleagues from Australia had produced the high-quality wafer and sent it to HZB. The thin film of germanium facilitates the growth of gallium arsenide crystals because the lattice constants of germanium and gallium arsenide are almost identical. They etched deep trenches into these wafers at intervals of a few micrometres until only a series of fine silicon columns topped with germanium remained on the substrate. Gallium arsenide was then deposited using metal organic vapour-phase epitaxy (MOVPE). In this way, both gallium and arsenic atoms were systematically deposited onto each germanium-capped silicon tower, forming a tiny, almost-perfect crystal. "The germanium acts like a crystallisation nucleus," explains Schmitt who is the first author of the study. The nano-architecture looks spectacular under the electron microscope. At first glance, it seems as if you can see a cube on the tip of each silicon needle. At second glance, it becomes apparent that it is actually a rhombic dodecahedron – with each of the twelve surfaces an identical rhombus.



Intensity distribution of the six optical modes in the rhombic dodecahedron is shown along two rectangular cross-sectional planes.

Decisive parameters: geometry and size

This nano-structure exhibits unusually high optical emission after excitation with a laser, especially in the near-infrared region. "As the GaAs crystals grow, germanium atoms also become incorporated into the crystal lattice," Schmitt explains. This incorporation of germanium leads to additional discrete energy levels for charge carriers that emit light when falling back to their original levels. The light is then amplified by means of optical resonances in the highly symmetrical nanocrystal, and the frequency of these resonances can be controlled by the size and geometry of the crystals. A large number of these so-called photonic resonances could be detected in the experiment, which also agree well with numerical calculations. "Because the optical and electronic properties of semiconductors can be strongly modified by nanostructuring, such nano-architectures are well suited for developing novel sensors, light-emitting diodes and solar cells," says Schmitt. *arö*

Advanced Optical Materials, 2018 (DOI: 10.1002/adom.201701329): Germanium-template-assisted integration of gallium arsenide nanocrystals on silicon: a versatile platform for modern optoelectronic materials; S. W. Schmitt et. al.

40-YEAR CONTROVERSY IN SOLID-STATE PHYSICS RESOLVED

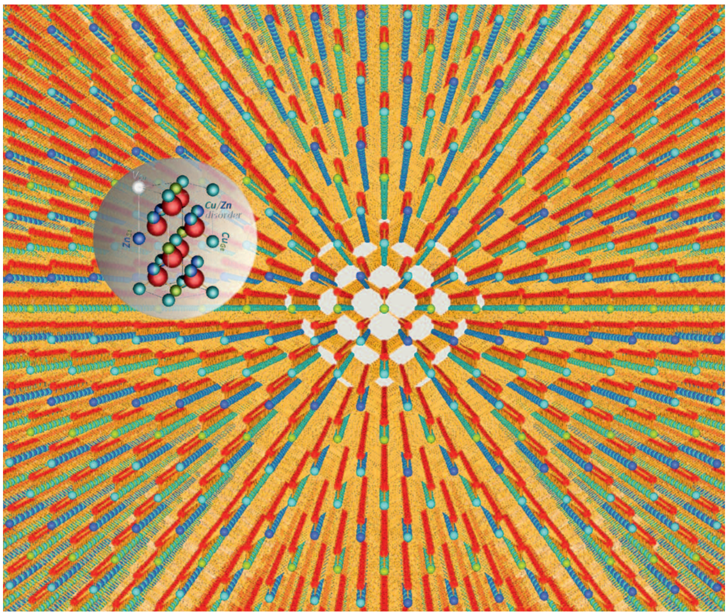
An international team at BESSY II headed by Prof. Oliver Rader has shown that the puzzling properties of samarium hexaboride do not stem from the material being a topological insulator, as it had been proposed to be. Theoretical and initial experimental work had previously indicated that this material, which becomes a Kondo insulator at very low temperatures, also possessed the properties of a topological insulator. The team has now published a compelling alternative explanation. *arö*

Nature Communication, 2018 (DOI: 10.1038/s41467-018-02908-7): Samarium hexaboride is a trivial surface conductor; P. Hlawenka et. al.

GERMANIUM PROMISES BETTER KESTERITE SOLAR CELLS

Specific changes in the composition of kesterite-type semiconductors make it possible to improve their suitability as **absorber layers in solar cells**. A team at Helmholtz-Zentrum Berlin showed that this is particularly true for kesterites in which tin was replaced by germanium.

Kesterites are semiconductor compounds made of the elements copper, tin, zinc and selenium. These semiconductors can be used as an optical absorber material in solar cells, but so far have only achieved a maximum efficiency of 12.6 per cent, while solar cells made of copper-indium-gallium-selenide (CIGS) already attain efficiencies of over 20 per cent. Nevertheless, kesterites are considered interesting alternatives to CIGS solar cells because they consist of common elements, so that no supply bottlenecks are to be expected. A team led by Professor Susan Schorr at the HZB has now investigated a series of non-stoichiometric kesterite samples and shed light on the relationship between the composition and opto-electronic properties. During the synthesis of the samples at HZB, the tin atoms were replaced with germanium.



The picture shows the typical arrangement of cations in a kesterite-type structure. In the background, the crystal structure is shown, with a unit cell highlighted.

Neutron diffraction at BER II

The researchers then investigated these samples using neutron diffraction at BER II. Copper, zinc and germanium can be distinguished from each other particularly well with this method, and their positions can be located within the crystal lattice. The result: kesterites with a slightly copper-poor and zinc-rich composition found in solar cells with the highest efficiencies also have the lowest concentration of point defects as well as the lowest disorder of copper–zinc. The more the composition was enriched with copper, the higher the concentration was of other point defects considered to be detrimental to the performance of solar cells. Further investigations showed that the energy band gap depends on the composition of the kesterite powder samples.

“This band gap is a characteristic of semiconductors and determines which frequencies of light release charge carriers within the material,” explains René Gunder, first author of the work. “We now know that germanium increases the optical band gap, allowing the material to convert a greater proportion of sunlight into electrical energy.” And, Schorr explains, “we are convinced that these kinds of kesterites are not only suitable for solar cells, but can also be considered for other applications. Kesterites acting as photocatalysts might be able to split water into hydrogen and oxygen using sunlight, and to store solar energy in the form of chemical energy.”

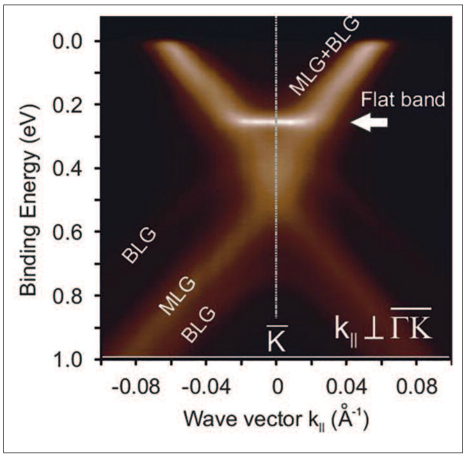
arö

CrystEngComm, 2018 (DOI: 10.1039/c7ce02090b): Structural characterization of off-stoichiometric kesterite-type $Cu_2ZnGeSe_4$ compound semiconductors: From cation distribution to intrinsic point defect density; R. Gunder, J. A. Márquez-Prieto, G. Gurieva, T. Unold and S. Schorr

GRAPHENE ON THE WAY TO SUPERCONDUCTIVITY

Scientists at HZB have probed the **band structure of double layers of graphene** at BESSY II with extremely high-resolution ARPES. They have identified a flat area at a surprising location that could generate a certain form of superconductivity.

Carbon atoms have diverse possibilities to form bonds. Pure carbon can therefore occur in many forms: as diamond, graphite, nanotubes, football-shaped molecules, or the honeycomb-net with hexagonal meshes known as graphene. This exotic, strictly two-dimensional material is an excellent conductor of electricity, but is not a superconductor. However, that might change. In April 2018, a group at Massachusetts Institute of Technology (MIT) showed that it is possible to generate a form of superconductivity in a system of two layers of graphene under very specific conditions. To do so, the two hexagonal nets must be twisted against each other by exactly the magic angle of 1.1 degree. Under this condition, a flat band forms in the electronic structure. The preparation of samples from two layers of graphene with such an exactly adjusted twist is complex, and not suitable for mass production.



The data show that in the case of the two-layer graphene, a flat part of its band structure is only 200 millielectronvolts below the Fermi energy.

Two graphene layers exactly on top of each other

But there is another, much simpler method of flat band formation. This was demonstrated by a group at HZB led by Prof. Oliver Rader and Dr. Andrei Varykhalov investigating at BESSY II. The samples were provided by Prof. Thomas Seyller of TU Chemnitz. There, they are made in a process that is also suitable for producing larger areas and greater quantities: a silicon carbide crystal is heated until silicon atoms evaporate from its surface, depositing first a single layer of graphene on the substrate, and then a second layer of graphene. The two graphene layers are not twisted against each other, but lie exactly on top of each other.

The insight came only with high resolution

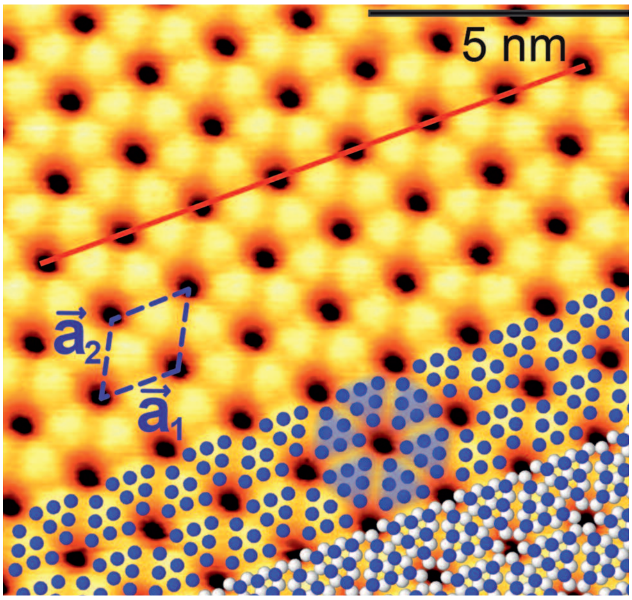
At BESSY II, the physicists were able to scan the so-called band structure of the sample. This band structure provides information on how the charge carriers are distributed among the quantum-mechanically permitted states and which charge carriers are available for transport at all. Angle-resolved photoemission spectroscopy (ARPES) at BESSY II enables such measurements with extremely high resolution. Via an exact analysis of the band structure, they identified an area that had previously been overlooked. "The double layer of graphene has been studied before because it is a semiconductor with a band gap," explains Varykhalov. "But on the ARPES instrument at BESSY II, the resolution is high enough to recognise the flat area next to this band gap."

"It is an overseen property of a well-studied system," first author Dr. Dmitry Marchenko points out: "It was previously unknown that there is a flat area in the band structure in such a simple well-known system." This flat area is a prerequisite for superconductivity but only if it is situated exactly at the so-called Fermi energy. In the case of the two-layer graphene, its energy level is only 200 millielectronvolts below the Fermi energy, and it is possible to raise the energy level of the flat area to the Fermi energy either by doping with foreign atoms or by applying an external voltage, the so-called gate voltage. The physicists have found that interactions between the two graphene layers and between graphene and the silicon carbide lattice are jointly responsible for the formation of the flat band area. "We can predict this behaviour with very few parameters and could use this mechanism to control the band structure," adds Rader. *arö*

Science Advances, 2018 (DOI: 10.1126/sciadv.aau0059): Extremely Flat Band in Bilayer Graphene; D. Marchenko et. al.

BLUE PHOSPHORUS – MAPPED AND MEASURED FOR THE FIRST TIME

Until recently, the existence of “blue” phosphorus was pure theory. Now, an HZB team has **examined samples of blue phosphorus at BESSY II** for the first time. This exotic phosphorus modification is an interesting candidate for new optoelectronic devices.



The scanning tunnelling microscope image shows blue phosphorus on a gold substrate. The calculated atomic positions of the slightly elevated phosphorous atoms are shown in blue, the lower-lying ones in white. Groups of six elevated phosphorous atoms appear as triangles.

The element phosphorus can exist in various allotropes and changes its properties with each new form. So far, red, violet, white and black phosphorus have been known. Some phosphorus compounds are essential for life, while white phosphorus is poisonous and inflammable and black phosphorus – on the contrary – is particularly robust. Now, another allotrope has been identified. In 2014, a team from Michigan State University, USA, performed model calculations that predicted that “blue phosphorus” should also be stable. In this form, the phosphorus atoms arrange in a honeycomb structure similar to graphene, except not completely flat but regularly “buckled”. Model calculations showed that blue phosphorus is not a narrow gap semiconductor like black phosphorus in the bulk but it does possess the properties of a semiconductor with a rather large band gap of two electronvolts. This large gap, which is seven times larger than in bulk black phosphorus, is important for optoelectronic applications.

Band structure influenced by the substrate

In 2016, blue phosphorus was successfully stabilised on a gold substrate by evaporation. Nevertheless, only now do we know for certain that the resulting material is indeed blue phosphorus. To this end, a team from HZB led by Dr. Evangelos Golias has probed the electronic band structure of the material at BESSY II. They were able to measure by angle-resolved photoelectron spectroscopy the distribution of electrons in its valence band, setting the lower limit for the band gap of blue phosphorus.
They found that the P atoms do not arrange themselves independently of the gold substrate but try to adjust to the spacings of the Au atoms. This distorts the corrugated honeycomb lattice in a regular manner, which in turn affects the behaviour of electrons in blue phosphorus. As a result, the top of the valence band that defines the one end of the semiconducting band gap agrees with the theoretical predictions, but is somewhat shifted.

Outlook: optoelectronic applications

“So far, researchers have mainly used bulk black phosphorus to exfoliate atomically thin layers,” Prof. Oliver Rader, head of the HZB department Materials for Green Spintronics explains. “These also show a large semiconducting band gap but do not possess the honeycomb structure of blue phosphorus and, above all, cannot be grown directly on a substrate. Our work not only reveals all the material properties of this novel two-dimensional phosphorus allotrope but highlights the impact of the supporting substrate on the behaviour of electrons in blue phosphorus, an essential parameter for any optoelectronic application.”

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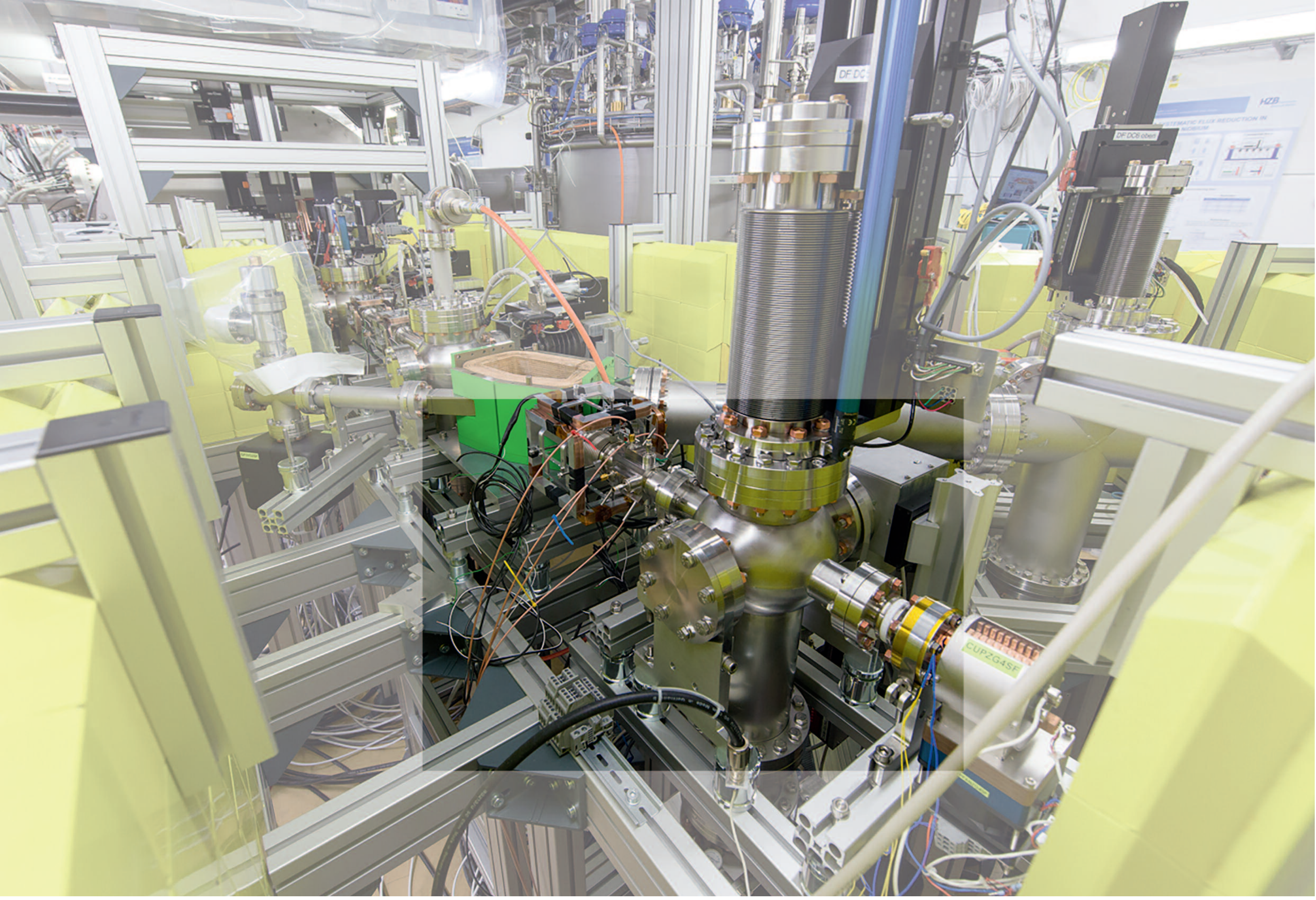
Nano Letters, 2018 (DOI:10.1021/acs.nanolett.8b01305): Band renormalization of blue phosphorus on Au(111); E. Golias, M. Krivenkov, A. Varykhalov, J. Sanchez-Barriga and O. Rader



DEVELOPING METHODS FOR RESEARCH AT HZB'S LARGE-SCALE FACILITIES

News in brief from HZB

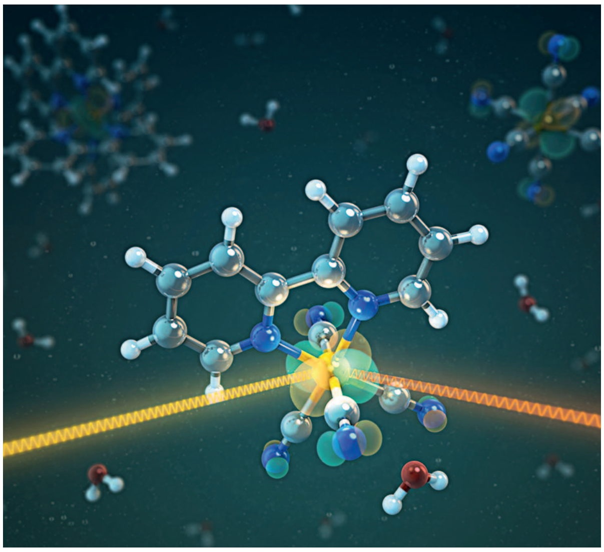
At the **EDDI beamline at BESSY II**, an HZB team headed by Dr. Francisco Garcia-Moreno developed an ingenious precision rotary table and combined it with especially fast optics. This enabled them to record the formation of pores in metal grains during foaming processes at 25 tomographic images per second – a world record for 3D tomographic images. The formation of pores in granules is a question of practical relevance because they are expected to fill complicated shapes better during the foaming process than foams manufactured from a block of metal. The resilience of the moulded part depends on the close bonding of the grains during foaming *(Journal of Synchrotron Radiation, 2018; DOI: 10.1107/S1600577518008949).*

A comprehensive overview of **neutron-based imaging processes** has been published by a team of researchers at HZB and the European Spallation Source (ESS). The authors report on the latest developments in neutron tomography, illustrating the possible applications with examples of this method. Neutrons can penetrate deep into a sample without destroying it. In addition, neutrons can distinguish between lightweight elements such as hydrogen and lithium. Neutron tomography has facilitated breakthroughs in such diverse areas as art history, battery research, dentistry, energy materials, industrial research, magnetism, palaeobiology and plant physiology *(Materials Today, 2018; DOI: 10.1016/j.mattod.2018.03.001).*

TRANSITION METAL COMPLEXES: MIXED WORKS BETTER

A team at BESSY II has investigated how various iron-complex compounds process energy from incident light. They were able to show why certain compounds have the potential to **convert light into electrical energy**. The results are important for the development of organic solar cells.

Transition-metal complexes is a slightly cumbersome name for a class of molecules with important properties, where an element from the group of transition metals sits in the centre. The outer electrons of the transition-metal atom are located in cloverleaf-like extended d-orbitals that can be easily influenced by external excitation. Some transition-metal complexes act as catalysts to accelerate certain chemical reactions, and others can even convert sunlight into electricity. The well-known dye solar cell developed by Michael Graetzel (EPFL) in the 1990s is based on a ruthenium complex.
However, it has not yet been possible to replace the rare and expensive transition metal ruthenium with a less expensive element such as iron. This is astonishing because the same number of electrons is found on the extended outer d-orbitals of iron. Sadly, excitation with light from the visible region does not release long-lived charge carriers in most of the iron complex compounds investigated so far.



The illustration shows a molecule with an iron atom at its centre, bound to four CN groups and a bipyridine molecule. The highest occupied iron orbital is shown as a green-red cloud. As soon as a cyan group is present, the outer iron orbitals are observed to delocalise so that electrons are also densely present around the nitrogen atoms.

Insights by RIXS at BESSY II

A team at BESSY II has now investigated this question in more detail. The group headed by Prof. Alexander Föhlisch has systematically irradiated different iron-complex compounds in solution using soft X-ray light. They were able to measure how much energy of this light was absorbed by the molecules using a method named resonant inelastic X-ray scattering, or RIXS. They investigated complexes in which the iron atom was surrounded by either bipyridine molecules or cyan groups (CN), as well as mixed forms in which each iron centre is bound to one bipyridine and four cyan groups.
The team members worked in shifts for two weeks in order to obtain the necessary data. The measurements showed that the mixed forms, which had hardly been investigated so far, are particularly interesting: in the case where iron is surrounded by three bipyridine molecules or six cyan groups (CN), optical excitation leads to only a short-term release of charge carriers, or to none at all. This situation only changes once two of the cyano groups are replaced by a bipyridine molecule. “Then we can see with the soft X-ray excitation how the iron 3d orbitals delocalise onto the cyan groups, while at the same time the bipyridine molecule can take up the charge carrier,” explains Raphael Jay, first author of the study whose doctoral work is in this field.
The results show that inexpensive transition-metal complexes could also be suitable for use in solar cells – if they are surrounded by suitable molecule groups. Accordingly, there is still a rich field here for future material development.

arö

Physical Chemistry Chemical Physics, 2018 (DOI: 10.1039/c8cp04341h): The nature of frontier orbitals under systematic ligand exchange in (pseudo-)octahedral Fe(II) complexes; R. M. Jay, S. Eckert, M. Fondell, P. S. Miedema, J. Norell, A. Pietzsch, W. Quevedo, J. Niskanen, K. Kunnus and A. Föhlisch

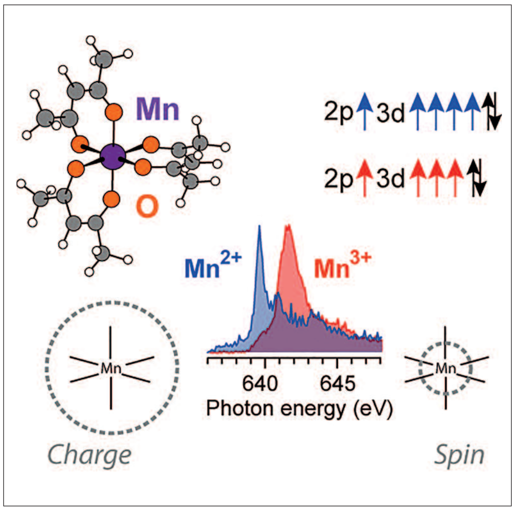
INSIGHT INTO ELECTRONIC STATES DURING CATALYSIS

An international team succeeded at BESSY II in investigating electronic states of a transition metal in detail and drawing reliable conclusions on their catalytic effect from the data. These results are helpful for the development of **future applications of catalytic transition-metal systems**.

Many important processes in nature depend on catalysts, which are atoms or molecules that facilitate a reaction but emerge from it themselves unchanged. One example is photosynthesis in plants, which is only possible with the help of a protein complex comprising four manganese atom sites at its centre. Redox reactions, as they are referred to, often play a pivotal role in these types of processes. The reactants are reduced through the uptake of electrons or oxidised through their release. Catalytic redox processes in nature and industry often only succeed when suitable catalysts are used, where transition metals provide an important function.
These transition metals and in particular their redox or oxidation state can be examined particularly well using soft X-rays because electronic states can be measured precisely using X-ray spectroscopy. In what is known as L-edge absorption spectroscopy, electrons from the 2p shell of the transition metal are excited so that they occupy free d-orbitals. An energy difference can be determined from the X-ray absorption spectrum that reflects the oxidation state of the molecule or the catalyst in a known way. However, exactly where the electrons are absorbed or released by the catalyst during a redox reaction, i.e. exactly how the charge density in the catalyst varies with oxidation state, was previously difficult to verify. This was mainly due to the lack of reliable methods for the theoretical description of charge densities in catalyst molecules in ground and excited states, and to the difficulty in obtaining reliable experimental data. If the transition metals are located in larger complex organic molecule complexes, as they typically are for real redox catalysts, their study becomes extremely difficult because the X-rays cause damage to the sample.

Different oxidation states examined

Now for the first time, an international team from Helmholtz-Zentrum Berlin, Uppsala University, Lawrence Berkeley National Laboratory in Berkeley, Manchester University and the SLAC National Accelerator Laboratory at Stanford University has succeeded in studying manganese atoms in different oxidation states – i.e. during different stages of oxidation – in various compounds through in operando measurements at BESSY II. To accomplish this, Philippe Wernet and his team introduced the samples into various solvents, examined jets of these liquids using X-rays, and compared their data against novel calculations from Marcus Lundberg's group at Uppsala University. “We succeeded in determining how – and above all why – the X-ray absorption spectra shift with the oxidation states,” says theoretician Marcus Lundberg.
“We combined a novel experimental set-up with quantum chemical calculations. In our opinion, we have achieved a breakthrough in the understanding of organometallic catalysts,” says Wernet. “For the first time, we were able to empirically test and validate calculations for oxidation and reduction that do not take place locally on the metal, but instead on the entire molecule.” *arö*



Manganese compounds also play a role as catalysts in photosynthesis.

Angew. Chem. Int. Ed. 2017, Vol. 56, Issue 22, 6088-609 (DOI: 10.1002/anie.201700239): Ultrafast Independent N-H and N-C Bond Deformation Investigated with Resonant Inelastic X-ray Scattering; S. Eckert, J. Norell, P. S. Miedema, M. Beye, M. Fondell, W. Quevedo, B. Kennedy, M. Hantschmann, A. Pietzsch, B. Van Kuiken, M. Ross, M. P. Minitti, S. P. Moeller, W. F. Schlotter, M. Khalil, M. Odelius and A. Föhlisch

NEUTRONS SCAN MAGNETIC FIELDS INSIDE SAMPLES

With a newly developed neutron tomography technique, an HZB team has been able to map for the first time magnetic field lines inside materials at the BER II research reactor. **Tensorial neutron tomography** promises new insights into superconductors, battery electrodes and other energy-related materials.

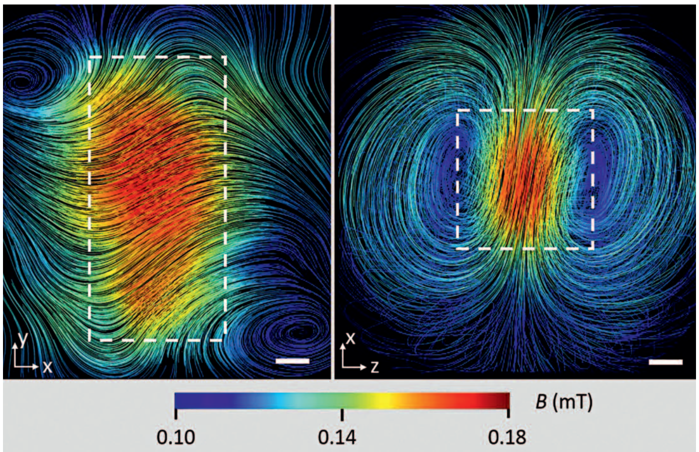
Measuring magnetic fields inside samples has only been indirectly possible up to now. Magnetic orientations can be scanned with light, X-rays or electrons – but only on the surfaces of materials. Neutrons, on the other hand, penetrate deeply into the sample and, thanks to their own magnetic orientation, can provide precise information about the magnetic fields inside. So far, however, it has only been possible to roughly map the variously aligned magnetic domains using neutrons, but not the vector fields (directions and strengths) of the magnetic fields inside samples.

A team led by Dr. Nikolay Kardjilov and Dr. Ingo Manke at HZB has now developed a new method for measuring the magnetic field lines inside massive, thick samples. For tensorial neutron tomography, they employ spin filters, spin flippers and spin polarisers that allow only neutrons with mutually aligned spins to penetrate the sample. When these spin-polarised neutrons encounter a magnetic field inside, the field excites the neutron spins to precess, so that the direction of the spin polarisation changes, allowing conclusions to be drawn about the field lines encountered.

3D image calculated with new TMART algorithm

The newly developed experimental method enables a three-dimensional image of the magnetic field inside the sample to be calculated using nine individual tomographic scans, each with a different neutron spin setting. A highly complex mathematical tensor algorithm was newly developed for this purpose by Dr. André Hilger at HZB, and was christened TMART. The experts tested and evaluated the new method on well-understood samples. Subsequently, they were able to map the complex magnetic field inside superconducting lead for the first time.

The sample of solid, polycrystalline lead was cooled to 4 kelvins (lead becomes superconducting below 7 kelvins) and exposed to a magnetic field of 0.5 milliteslas. Although the magnetic field is displaced from the interior of the sample due to the Meissner effect, magnetic flux lines nevertheless remain attached to the (non-superconducting) grain boundaries of the polycrystalline sample. These flux lines do not disappear even after the external field has



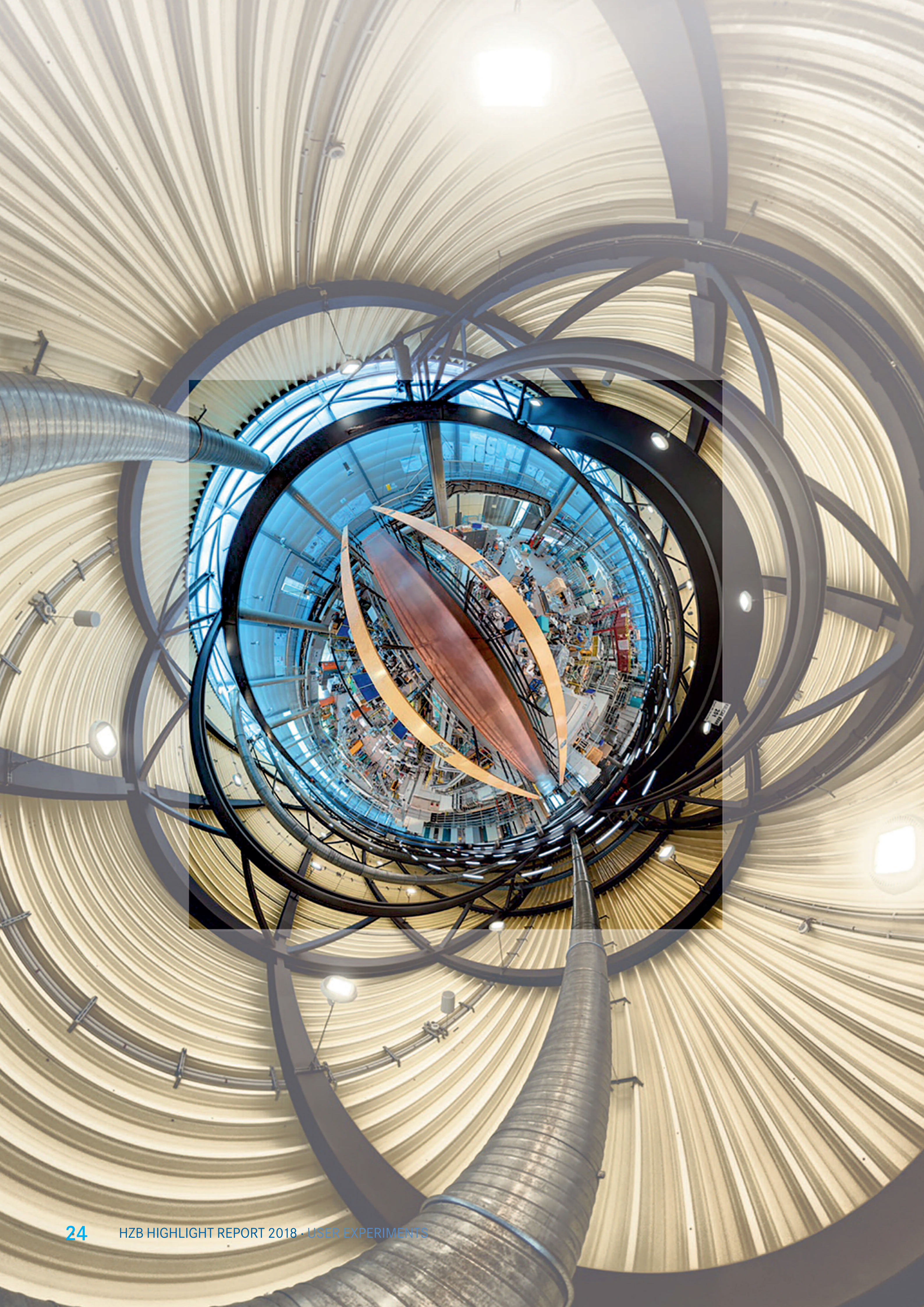
Shown are the magnetic flux lines inside a superconducting sample of lead in two different directions. The scale bar is five millimetres.

been switched off because they have previously induced currents inside the superconducting crystal grains, which now maintain these fields. “For the first time, we can make the magnetic vector field visible in three dimensions in all its complexity within a massive material,” says HZB physicist Manke. “Neutrons can simultaneously penetrate massive materials and detect magnetic fields. There is currently no other method that can accomplish this.”

A wide range of industrial applications

Magnetic tensor tomography is non-destructive and can achieve resolutions down to the micrometre range. The areas of application are extremely diverse. They range from the mapping of magnetic fields in superconductors and the observation of magnetic phase transitions to material analysis, which is also of great interest for industry: Field distributions in electric motors and metallic components can be mapped and current flows in batteries, fuel cells or other propulsion systems can be visualised with this method. *arö*

Nature Communications, 2018 (DOI: 10.1038/s41467-018-06593-4): Tensorial Neutron Tomography of Three-Dimensional Magnetic Vector Fields in Bulk Materials; A. Hilger et. al.



USER EXPERIMENTS

At the **neutron source BER II**, a team from the Bundesanstalt für Materialforschung und -prüfung (BAM) analysed the residual stress of ferromagnetic steel weld seams. Neutron experiments are still the method of choice for very precisely determining the existing residual stress deep within materials. Large differences in residual stress equate to high overall stress in a material, which can even ultimately tear it apart. The researchers first studied the very weak magnetic fields of weld seams made of a ferromagnetic steel. Using special magnetic sensors, they conducted measurements with a high sensitivity and with a local resolution in the tenth of a micrometre range. Next, the researchers identified the different material properties of the weld seams. Thanks to their results, we are coming closer to the vision of early detection of important material changes using magnetic field sensors before any cracks arise at all – and even cheaply and nondestructively *(Journal of Nondestructive Evaluation, DOI: 10.1007/s10921-018-0522-0)*.

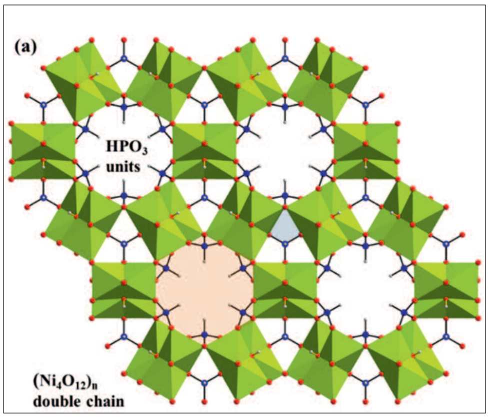
With **experiments based on extremely short X-ray pulses,** a team of researchers from HZB and the University of Potsdam has investigated heat transport in a model system comprising nanometre-thin metallic and magnetic layers. Similar systems are candidates for future high-efficiency data storage devices that can be locally heated and rewritten by laser pulses (Heat-Assisted Magnetic Recording). The scientists' measurements revealed that the heat is distributed a hundred times slower than expected in the model system, which consisted of gold and nickel. "With this experimental set-up, we were able to show that it is worthwhile analysing these kinds of transport processes in the temporal domain," says Prof. Matias Bargheer of the University of Potsdam, who heads a Joint Research Group on ultrafast dynamics at the HZB. With a deeper understanding of the transport processes, scientists could develop heat-assisted magnetic recording techniques that can be managed with minimal input energy *(Nature Communications 9, 2018, 3335 (DOI: 10.1038/s41467-018-05693-5)*.

News in brief from HZB

A SUPERCATALYST FOR WATER ELECTROLYSIS

Scientists from Berlin have created a new kind of **crystal made of nickel and phosphorus**. Experiments at BESSY II prove that its extraordinary properties make the material a good catalyst for the electrochemical production of hydrogen.

The process to obtain hydrogen from the electrochemical splitting of water requires highly active catalysts. "So far, this is mostly done using precious metals," says Prof. Holger Dau, Head of the Biophysics and Photosynthesis Workgroup at Freie Universität Berlin. The cathode where the hydrogen forms is often made of platinum. At the anode, where oxygen is formed as the second product of electrolysis, the reaction accelerators are indium or ruthenium. What makes each metal special is what physicists and electrochemists call the overpotential: this is the amount of energy that is required – in addition to the minimum chemical binding energy to be applied – to split water into its elemental components. "If the overpotential is large, the process is inefficient," Dau says. That means a lot of energy is lost, unused. Many precious metals, it turns out, stand out for having a very small overpotential, which is why they are in such high demand for electrolysis.



The nickel-oxygen octahedrons (green) are linked via oxygen atoms (red) with phosphorus atoms (blue) so as to form hexagonal channels.

High efficiency and long stability

However, "those elements are rare and expensive," Dau asserts. "That means large-scale hydrogen production is not possible." Accordingly, researchers are looking for alternative materials that have similarly favourable properties as platinum and co. An interdisciplinary team of Freie Universität and Technische Universität Berlin, of which Dau is a member, has now found one: the scientists have produced a novel crystalline material that "shines" for many of the same advantageous properties – and even outperforms the expensive precious metals in some ways.

The compound, based on nickel and phosphorus, not only has a higher energy efficiency; it is also extremely stable. "That allows long operation in electrolysis without having to change the catalyst," says Dau. Unlike many other materials, the structure of the material, characterised by phosphite ions in the nickel crystal lattice, does not change over time. It is catalytically active from the outset and – unlike precious metals – is bifunctional, meaning it can serve as both cathode and anode.

Tracking down the optimum catalyst

In order to find out how the useful characteristics of this nickel-phosphite compound can be properly explained, the researchers studied the material using X-ray spectroscopy at BESSY II. "The measurements reveal an extraordinary structure," Dau reports. "In the middle of each eight-sided crystal unit sits a nickel atom; on the sides are oxygen atoms." The physicists suspect that channels form between them, through which protons – the atomic nuclei of hydrogen – can travel particularly easily.

The development of the new material is attributable to the researchers in the group of Prof. Matthias Diess of the Institute of Chemistry, Metalorganics and Inorganic Materials of TU Berlin. Driven by the promising results with nickel-phosphite, they collaborated with physicists led by Holger Dau to create other materials with a similarly unusual crystalline structure and even more favourable properties. Their aim: "We want to better understand catalysts and find an optimum compound for obtaining the alternative fuel hydrogen out of simple water," Dau asserts. This way, the researchers could provide a substantial boost to the energy turnaround.

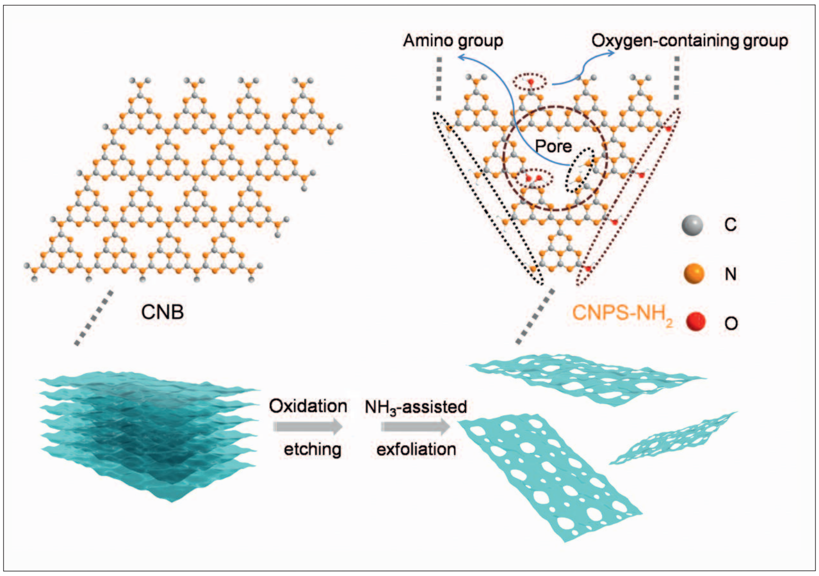
rb

Energy Environ. Sci., 2018, 11, 1287-1298 (DOI: 10.1039/C7EE03619A): A structurally versatile nickel phosphite acting as a robust bifunctional electrocatalyst for overall water splitting; P. W. Menezes, C. Panda, S. Loos, F. Bunschei-Bruns, C. Walter, M. Schwarze, X. Deng, H. Dau and M. Driess

NANOSTRUCTURING INCREASES EFFICIENCY OF METAL-FREE PHOTOCATALYSTS

A team at Tianjin University in China, in collaboration with a group at HZB, has increased the **catalytic efficiency of polymeric carbon nitrides** by a factor of eleven through a simple process. These low-cost and metal-free materials could be used for the production of hydrogen from solar energy.

One of the major challenges of the energy transition is to supply energy even when the sun is not shining. Hydrogen production by splitting water with the help of sunlight could offer a solution. Hydrogen is a good energy storage medium and can be used in many ways. However, water does not simply split by itself. Catalysts are needed, for instance platinum, which is rare and expensive. Research teams the world over are looking for more economical alternatives. A team headed by Dr. Tristan Petit from HZB, together with colleagues led by Prof. Bin Zhang from Tianjin University, China, has made important progress using a well-known class of metal-free photocatalysts.



A heat treatment of polymeric carbon nitrides (PCN) produced samples consisting of individual nanolayers with large pores containing different amino groups with specific functionalities.

Bin Zhang and his team specialise in the synthesis of polymeric carbon nitrides (PCN), which are considered good candidates as catalysts for hydrogen production. The PCN molecules form a structure that can be compared to thin layers of filo pastry dough: sheets of this material lie on top of each other, tightly packed together. The Chinese chemists have now succeeded in separating the individual sheets from each other by means of a relatively simple two-step heat treatment – the same way that puff pastry separates into individual crispy layers in the oven. The heat treatment produced samples consisting of individual nanolayers with large pores containing different amino groups with specific functionalities.

Deposition of amino groups

Petit and his team investigated a series of these PCN samples at BESSY II. “We were able to determine which amino and oxygenated groups had been deposited in the pores,” PhD student and co-first author of the publication Jian Ren explains. They could analyse how specific amino groups pull electrons to themselves, a particularly favourable property for splitting water, and how new oxygen-based defects were formed. When combined with nickel as a co-catalyst, those samples of nanostructured PCN actually exhibited record-breaking efficiency, eleven times that of normal PCN under visible light irradiation.

Soft X-ray spectroscopy is essential

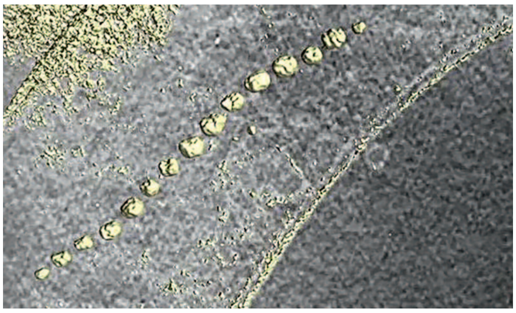
“This demonstrates that PCN is an interesting potential catalyst for solar-to-hydrogen production, approaching the efficiency of inorganic catalysts,” explains Petit, who is a Volkswagen Foundation Freigeist Fellow. “Furthermore, this work also shows that soft X-ray spectroscopies are essential tools for unravelling potential catalytically active sites on photocatalysts.” *red/arö*

Energy & Environmental Science, 2018 (DOI: 10.1039/C7EE03592F): Engineering oxygen-containing and amino groups into two-dimensional atomically-thin porous polymeric carbon nitrogen for enhanced photocatalytic hydrogen production; N. Meng, J. Ren, Y. Liu, Y. Huang, T. Petit and B. Zhang

BACTERIA WITH A MAGNETOTACTIC-SENSITIVE COMPASS

A cooperation of Spanish teams and experts at HZB have examined the **magnetic compass** of *Magnetospirillum gryphiswaldense* at BESSY II. Their results may be helpful in designing actuation devices for nanorobots and nanosensors for biomedical applications.

Bacteria exist in many shapes and with very different talents. Magnetotactic bacteria can even sense the earth's magnetic field by making use of magnetic nanoparticles in their interior that act as an internal compass. They are usually found in freshwater and marine sediments. One species, *Magnetospirillum gryphiswaldense*, is easily cultivated in the lab – with or without magnetic nanoparticles in their interior depending on the presence or absence of iron in the local environment. “So these microorganisms are ideal test cases for understanding how their internal compass is constructed,” explains Lourdes Marcano, a PhD student in physics at Universidad del Pais Vasco in Leioa, Spain.

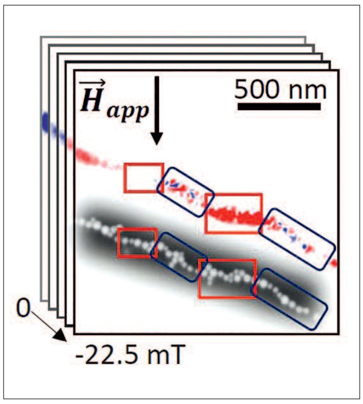


Magnetosomes form a chain inside the bacteria's cell, as shown by electron cryotomography (ECT).

Magnetospirillum cells contain a number of small particles of magnetite (Fe_3O_4), each approx. 45 nanometres wide. These nanoparticles, called magnetosomes, are usually arranged as a chain inside the bacteria. This chain acts as a permanent dipole magnet and is able to passively reorient the whole bacteria along the earth's magnetic field lines. “The bacteria exist preferentially at the oxy/anoxy transition zones,” Marcano points out, “and the internal compass might help them to find the best level in the stratified water column for satisfying their nutritional requirements.” The Spanish scientists examined the shape of the magnetosomes and their arrangement inside the cells using various experimental methods such as electron cryotomography.

Isolated chains examined at BESSY II

Samples of isolated magnetosome chains were analysed at BESSY II to investigate the relative orientation between a chain's direction and the magnetic field generated by the magnetosomes. “Current methods employed to characterise the magnetic properties of these bacteria require sampling over hundreds of non-aligned magnetosome chains. Using photoelectron emission microscopy (PEEM) and X-ray magnetic circular dichroism (XMCD) at HZB, we are able to “see” and characterise the magnetic properties of individual chains,” explains Dr. Sergio Valencia of HZB. “Being able to visualise the magnetic properties of individual magnetosome chains opens up the possibility of comparing the results with theoretical predictions.”



Experiments at BESSY II revealed how an external magnetic field changes the orientations of chain parts.

Indeed, the experiments revealed that the magnetic field orientation of the magnetosomes does not follow along the chain direction, as assumed up to now, but is slightly tilted. As the Spanish group's theoretical modelling suggests, this tilt might explain why magnetosome chains are not straight but rather helical in shape. A deeper understanding of the mechanisms determining the chain shape is very important, the scientists point out. Nature's inventions could inspire new biomedical solutions such as nanorobots propelled by flagella systems in the direction provided by their magnetosome chain.

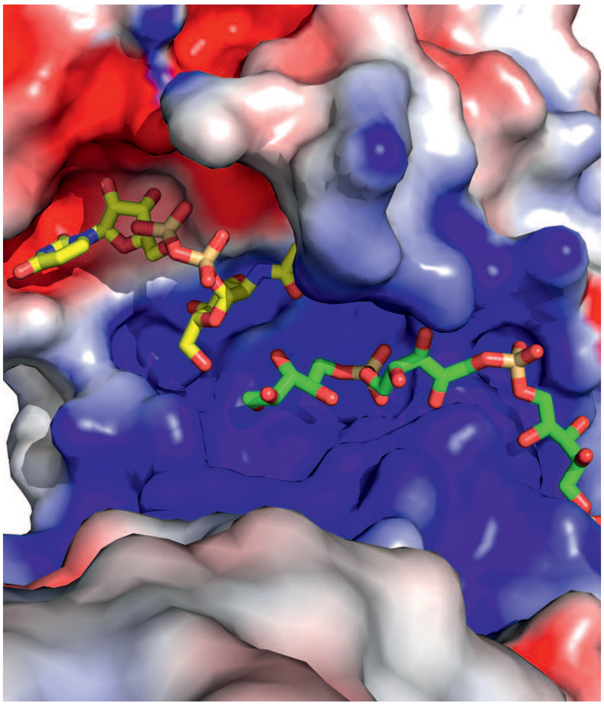
arö

Nanoscale, 2018 (DOI: 10.1039/C7NR08493E): Configuration of the magnetosome chain: a natural magnetic nanoarchitecture; I. Orue, L. Marcano, P. Bender, A. Garcıa-Prieto, S. Valencia, M.A. Mawass, D. Gil-Carton, D. Alba Venero, D. Honecker, A. Garcıa-Arribas, L. Fernandez Barquın, A. Muela, M.L. Fdez-Gubieda

TINY CHANGES WITH A DEADLY EFFECT

In many hospitals around the world, doctors are fighting a desperate battle: a whole range of antibiotics have become ineffective against infections with bacteria such as *Staphylococcus aureus*. Working with data from BESSY II, researchers have discovered the **reason behind this bacterium's antibiotic resistance**.

Methicillin-resistant *Staphylococcus aureus* bacteria, more familiarly known as MRSA bacteria, can cause infections that often prove fatal. By revealing microscopic details in the cell walls of these MRSA bacteria using X-ray structural analyses at BESSY II, Prof. Thilo Stehle und Dr. Yinglan Guo of the University of Tübingen have pushed open a door behind which a possibility of treating these highly dangerous infections in future years has come into sight.
The researchers noticed that a considerable portion of the dangerous MRSA pathogens themselves were infected by so-called bacteriophages, which are viruses that specifically target bacteria. "We are investigating these pathogens with everything we've got, from studies in mice to structural analyses with the data we gained from BESSY II, which let us track down individual atoms," Thilo Stehle explains. The researchers are currently especially interested in the cell walls of the bacteria. They are built as many layers of very large molecules made up of sugars and amino acids. Embedded into these layers are proteins and teichoic acids. The latter are chains of sugars and phosphates.

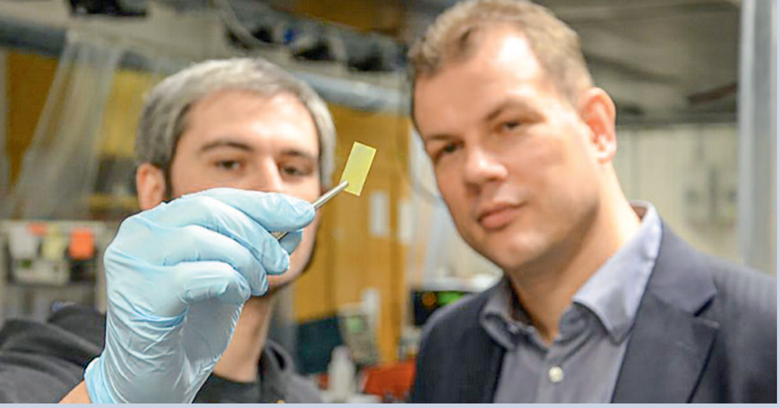


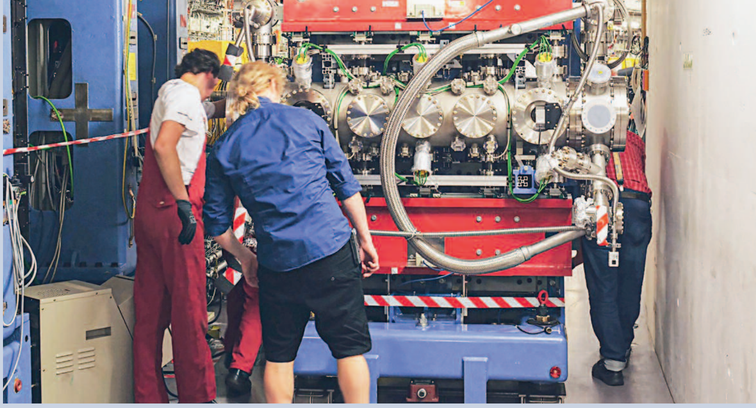
The model shows the TarP enzyme from a bacteria-targeting virus in the process of attaching a sugar molecule (yellow-red rods) onto a teichoic acid chain (green-red). This process makes the bacterium resistant to antibiotics.

Immune defences foiled

The bacteria possess an enzyme called TarS, which builds individual sugar molecules into these teichoic acids at specific sites (a process called glycosylation). In MRSA pathogens, however, this enzyme has been replaced by a very similar enzyme called TarP from the bacteria-eating viruses. At first glance, this TarP only seems to make one small difference: while TarS links the sugar molecule to the fourth carbon atom in a teichoic acid chain, TarP shifts the sugar to the third carbon atom in the chain. The consequences of this seemingly minor structural change are dramatic, as the researchers discovered when they injected both modifications of teichoic acid into mice. The animals' immune system was clearly able to detect the TarS-glycosylated teichoic acid very well and produced large amounts of antibodies against this version, meaning a targeted immune response to such a bacterial infection is normally possible. After injection with teichoic acids glycosylated by bacteriophage-TarP, however, the researchers detected only very small amounts of corresponding antibodies. "Apparently, this is how these bacteria evade the immune response," Stehle explains.
"Why the antibodies are produced less efficiently is what we will be investigating next," Stehle announces. If the researchers understand these processes, they might also find substances that block the bacteriophage TarP enzyme, and thus prevent this undermining of the immune defences. Then it might be possible to help the patient's organism fight off dangerous MRSA bacteria. *rk*

Nature, Vol. 563, 705–709, 2018 (DOI: 10.1038/s41586-018-0730-x): Methicillin-resistant *Staphylococcus aureus* alters cell wall glycosylation to evade immunity; D. Gerlach et. al.





Prof. Dr. Roel van de Krol (right), Head of the HZB Institute for Solar Fuels, and his team are researching the possibilities of storing solar energy chemically in the form of hydrogen and other fuels.

In September 2018, the new CPMU 17 undulator was built into the storage ring BESSY II to provide high-brightness X-rays in the tender X-ray region for the EMIL laboratory.

FACTS AND FIGURES ABOUT HZB

23

per cent of the 692 scientific employees at HZB at the end of 2018 were women. The proportion of women among all 1,169 employees was 30.5 per cent.

557

ISI- and SCOPUS-cited papers were published by scientists of HZB in 2018.

4,700

visitors attended the „Long Night of Science" at HZB in Berlin-Adlershof. They informed themselves about the operation and scientific research at BESSY II and discussed the prospects of solar energy with scientists working at HZB.

305

cooperatives were maintained by HZB with other scientific establishments at the end of 2018 – a considerable increase compared with the previous year (252).

21

young students from 11 countries worked at HZB for eight weeks during the summer of 2018 as part of the popular Summer Programme. As always, they were supervised by enthusiastic HZB researchers.

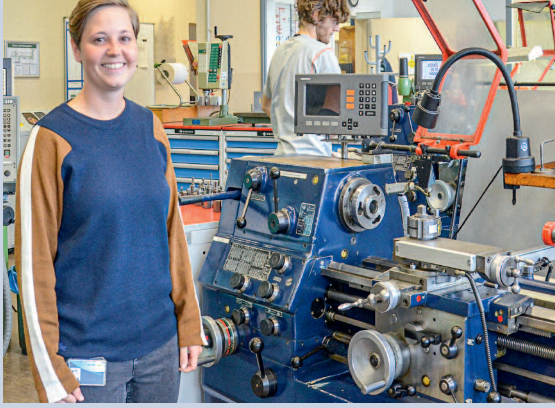
15,566

shifts of eight hours were dedicated to scientific research for 2,241 users from 31 countries at 27 beamlines with 36 experimental stations of the storage ring facility BESSY II in 2018.

19.94

million euros in third-party funding went to HZB in 2018. This included around 4.39 million euros for contract research, 3.92 million euros for services for third parties, around 4.18 million euros in project funding from the Federal government, and around 2.35 million euros from the European Union.

The synchrotron source BESSY is being upgraded into a variable-pulse-length storage ring (VSR) within the scope of the HZB Strategy 2020+ project. When finished, researchers will be able to work with bright X-ray pulses of different durations.



HZB expertly prepares young people for the working world: Milena Meschenmoser completed her training as a precision mechanic as Best in State of Berlin in 2018.

143

PhD students were supervised at HZB in 2018. The number of theses completed in the same year was 32.

4.66

million euros were received by HZB for technology transfer in 2018. Around 1.61 million euros came from research and development partnerships and from R&D orders with domestic and international commercial enterprises, nearly one million euros from other R&D cooperatives. Another 2.09 million euros originated from infrastructure agreements.

9

young investigator groups were researching at HZB in 2018. All nine of these young investigator groups are in the POF fields “Renewable Energies” and “Energy Materials”.

8

patents were granted to HZB in 2018. At the end of the year, HZB’s portfolio amounted to 198 patents, 27 of which are objects of ongoing licence agreements. 11 invention disclosures from 2018 were evaluated by HZB or external technology experts with regard to their patentability and/or commercial exploitability.

75

cooperative partnerships between HZB and companies were newly established in 2018 alone. Thus the total number of ongoing cooperative partnerships with industry has further increased from 135 in the previous year to 153. Of these, nearly 19 per cent were cooperatives with companies from outside Germany and 16 per cent cooperatives with small to mid-sized businesses.

149

days over 13 reactor cycles were clocked for powered operation of the research reactor BER II in 2018. This equates to a total of 1,484 instrument days of regular operation on 10 instruments. 216 instrument days were needed for instrument development and maintenance. The remaining 1,269 experimental days were used for the experiments of internal and external guests.

3,500

school students experimented at the two School Labs in Wannsee and Adlershof in 2018. 60 per cent were from primary schools and the remaining students from secondary schools.

35

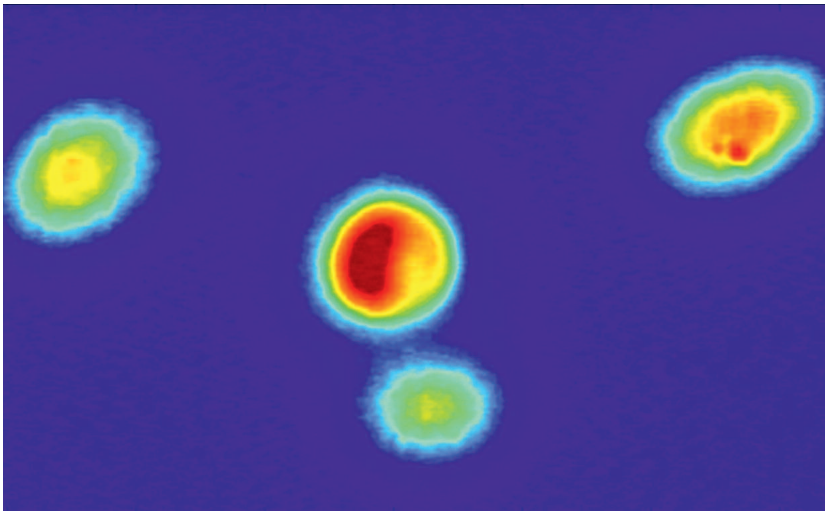
adolescents and young adults were receiving training at HZB at the end of 2018.

ACCELERATOR RESEARCH AND DEVELOPMENT

HZB is building an **APPLE II Undulator** for the SESAME synchrotron light source in Jordan, approximately 35 kilometres northwest of the capital Amman. SESAME stands for "Synchrotron Light for Experimental Science and Applications in the Middle East" and provides brilliant X-ray light for research purposes. The third-generation synchrotron radiation source became operational in 2017. Egypt, Iran, Israel, Jordan, Pakistan, the Palestinian Authority, Turkey and Cyprus are cooperating on this unique project to provide scientists from the Middle East with access to one of the most versatile tools for research.So far, SESAME has four beamlines and will now receive a fifth intended to generate "soft" X-ray light in the energy range between 70 eV and 1800 eV. This X-ray light is particularly suitable for investigating surfaces and interfaces of various materials, for observing certain chemical and electronic processes, and for non-destructive analysis of cultural artefacts. The new beamline will be constructed as the Helmholtz SESAME Beamline (HESEB) by HZB as well as the Helmholtz Centres DESY, Forschungszentrum Jülich, Helmholtz-Zentrum Dresden-Rossendorf (HZDR) and Karlsruhe Institute of Technology (KIT). The Helmholtz Association is investing 3.5 million euros in this project coordinated by DESY.

TWIN-ORBIT OPERATION SUCCESSFULLY TESTED AT BESSY II

Physicists at Helmholtz-Zentrum Berlin have been able to **store two separate electron beams in one storage ring**. The twin-orbit operation mode can serve users with different needs of the time structure of the photon pulses simultaneously.



A synchrotron source point image of a bending magnet of twin-orbit modus. The second orbit closes after three revolutions and winds around the standard orbit at the centre.

The first "Twin-Orbit User Test week" at BESSY II was a big success and can be considered an important step towards real user operation. Twin-Orbit operation mode also offers elegant options for the future project BESSY VSR. Twin Orbit operation mode makes use of non-linear beam dynamics and provides two stable and well-separated orbits for storing two electron beams in one storage ring. The bunch fill patterns of both orbits can be chosen, to some extent, independently so that normally incompatible user needs can be fulfilled simultaneously. For example, one orbit can be used to store a homogeneous multibunch fill to deliver high average brilliance for photon-hungry experiments, whereas only one single bunch is stored on the other orbit for timing experiments, providing a much lower pulse repetition rate.

First experiments in 2015

It is a long process from an idea to a real operational week, especially at a running multiuser facility. First studies of this mode already started in 2015 at the smaller ring, the Metrology Light Source (MLS), resulting in a successful user experiment with the Physikalisch Technische Bundesanstalt (PTB). In parallel, a group of HZB experts implemented and optimised this mode at BESSY II in single machine commissioning shifts. Important milestones have been the operation of a large number of insertion devices as well as the topping-up injection scheme to keep the stored current constant.
In 2017, a successful overnight run with topping-up injection and some participating beamlines gave confidence for a longer test week. The days of this "Twin-Orbit User Test week" were used for common experiments of machine group and beamline scientists in order to characterise this operational mode and generate feedback for further optimisation. During the nights and the entire weekend, 'normal' user time was scheduled with two different fill patterns (multibunch and single-bunch) on both orbits. The availability and stability of the synchrotron source were comparable to the current standard user mode and exceeded 99 per cent.

Elegant option for BESSY VSR

"There is still a lot of work to do but, nevertheless, this proof-of-principle week showed that a development towards a realistic user mode should be possible. And even more, for the future BESSY VSR project, it could be a very elegant way to separate short and long bunches," Prof. Andreas Jankowiak concludes.

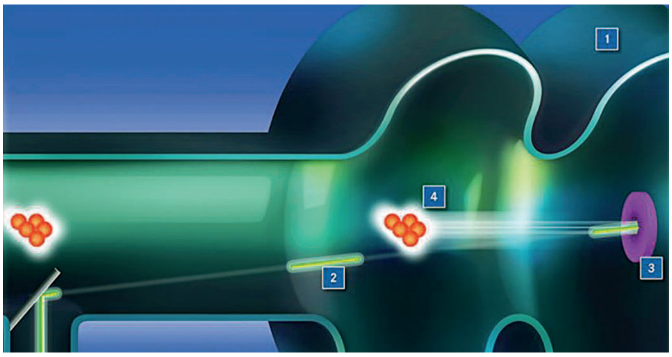
Dr. Paul Goslawski

Further information about the first experiment at http://accelconf.web.cern.ch/AccelConf/IPAC2015/papers/mopwa021.pdf and about the first test week in user operation at http://accelconf.web.cern.ch/AccelConf/ipac2017/papers/wepik057.pdf.

MILESTONE FOR BERLINPRO: PHOTOCATHODES WITH HIGH QUANTUM EFFICIENCY

A team at HZB has improved the manufacturing process of photocathodes and can now provide high-quantum-efficiency photocathodes for the **first electron beam for bERLinPro**.

Teams from HZB's Accelerator Physics and SRF groups are developing a superconducting linear accelerator featuring energy recovery (Energy Recovery Linac) as part of the bERLinPro project. It accelerates an intense electron beam that can be used for various applications – such as generating brilliant synchrotron radiation. Once used, the electron bunches are directed back into the superconducting linear accelerator, where they release almost all of their remaining energy. This energy is then available for accelerating new electron bunches.



The superconducting photoinjector system (1): the photocathode (3) is excited by a green laser (2) and emits electrons (4) which are accelerated in the superconducting RF cavity.

Intensive research has been going on for years to develop the worldwide unique key components required for this accelerator. Scientists and engineers at HZB have reached a very important stopover: from the interactions between the cathode, laser pulse and electric field inside the cavity, the first electrons have been produced and accelerated. The researchers have developed and built to testing maturity four essential components for producing the electron bunches: a potassium-caesium-antimonide semiconductor photocathode; a laser that fires light pulses of different wavelengths and durations at this cathode; a superconducting high-frequency cavity in which electromagnetic fields accelerate the bunches to near light speed; and a beam diagnostics beamline for precisely measuring the important beam parameters. These components have been combined together and tested successfully in the GunLab, a 75-square-metre laboratory.

Electron source: photocathode

Another crucial component in the design is the electron source. Electrons are generated by illuminating a photocathode with a green laser beam. The quantum efficiency is the term for how many electrons the photocathode material emits when illuminated at a certain laser wavelength and power. Bialkali antimonides exhibit a particularly high quantum efficiency in the region of visible light. However, thin films of these materials are highly reactive and therefore very sensitive, so they only work in an ultra-high vacuum. An HZB team headed by Martin Schmeißer, Dr. Julius Kühn, Dr. Sonal Mistry and Prof. Thorsten Kamps has greatly improved the performance of the photocathode so it is ready for use with bERLinPro. They modified the process for manufacturing the photocathodes of caesium-potassium-antimonide on a molybdenum substrate. The process delivers the desired high quantum efficiency and stability. Studies showed that the photocathodes do not degrade, even at low temperatures. This is a critical prerequisite for operation within a superconducting electron source, where the cathode must be operated at temperatures far below zero. The physicists were able to demonstrate this performance with detailed studies: even after its transport via the photocathode transfer system and introduction into the photo injector of the SRF, the quantum efficiency of the photocathode was still about five times higher than necessary to achieve the maximum electron-beam current needed for bERLinPro. "An important milestone for bERLinPro has been reached. We now have the photocathodes available to generate the first electron beam from our SRF photoinjector at bERLinPro in 2019," says Prof. Andreas Jankowiak, Head of the HZB Institute for Accelerator Physics. *arö*

Physical Review Accelerators and Beams, 2018 (DOI:10.1103/PhysRevAccelBeams.21.113401): Addressing challenges related to the operation of Cs-K-Sb photocathodes in SRF photoinjectors; M. Schmeisser et. al.

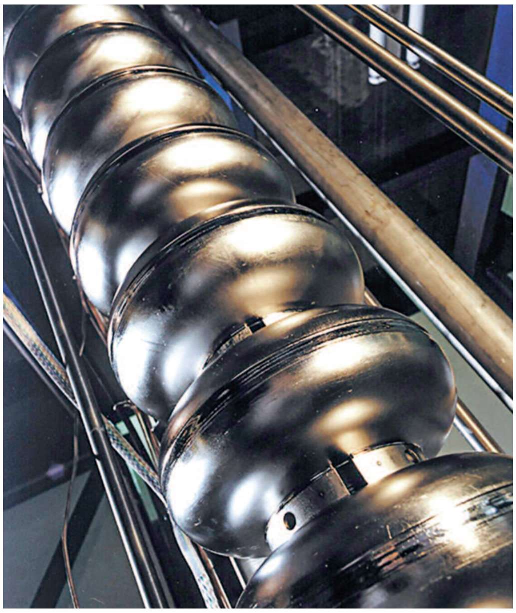
CAVITIES OF SUPERCONDUCTING NIOBIUM

In BESSY II, four cavities allow the electron bunches to recover the energy they radiated off as X-ray light. Teams are developing **cavities made out of superconducting niobium** for the future projects bERLinPro and BESSY VSR. The experience they are gaining from this will also shape the plans for BESSY III.

Cavities is the short name for cavity resonators that absorb and amplify certain oscillations or frequencies. Organ pipes are an acoustic example of this: at a certain pitch, sound inside them forms a standing wave – resonance. Large pipes amplify low notes, while short pipes amplify high notes. The cavities in BESSY II are excited by alternating electromagnetic fields. At the resonance frequency, electromagnetic waves arise inside the cavity. Electron bunches are directed through this alternating field. If they enter the cavity at precisely the moment when the field is undergoing maximum forward acceleration, they absorb energy. This process can also be compared to a swing which has to be pushed at the right time in order to give it more momentum. Inside the cavity, however, the electron bunches cannot only absorb energy but also give off energy.
Experts exploit this phenomenon for the energy recovery linear accelerator bERLinPro (Berlin Energy Recovery Linac Project). Once they have passed through the linac, the electron bunches are redirected back into the cavities – this time so that they give off their remaining energy to the alternating field. This energy is then available again for accelerating the next electron bunches. “For bERLinPro, however, we need to use superconducting cavities made of niobium, which can withstand very high fields but are still very good at dampening disruptive harmonic waves,” explains Prof. Jens Knobloch, Head of the HZB Institute SRF – Science and Technology. His team is responsible for developing the cavities and all associated components.

Pioneering work at HZB for high current cavities

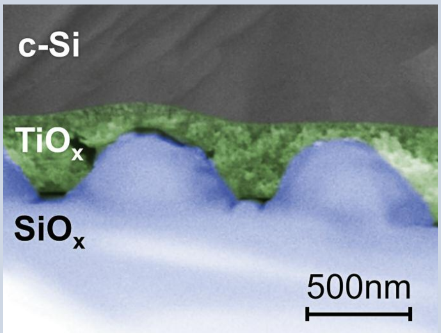
Similar cavities are already being used in a number of accelerators around the world. Yet the work being done at HZB is still pioneering: “We are developing the cavities with high currents in mind, and are working out how we can efficiently suppress unwanted oscillations,” explains Dr. Axel Neumann from Knobloch’s team. HZB has built up an extensive infrastructure for testing this over the past several months. This work will be of benefit in the upgrading of BESSY II into BESSY-VSR (variable-pulse-length storage ring). The most important element of BESSY VSR is the combination of two superconducting high-current cavities. With their resonant frequencies of 1.5 gigahertz and 1.75 gigahertz, they give rise to a so-called beating effect. This leads to an interesting phenomenon: when electron bunches travel through the double-cavity, some of them become compressed to one tenth of their size and others do not. The compressed electron bunches then give off ultrashort light pulses of around 1.5 picoseconds, while the others produce light pulses of around 15 picoseconds. This will give guest experimenters at BESSY VSR in the future a choice between the two durations. Accordingly, they will be able to use light pulses of the optimum duration for their experiment – at the customary full beam brightness.
The experience being gained from both projects is important for the future. “We can’t say yet what BESSY III will look like, exactly, but we are learning a great deal from these projects for the design and operation of novel cavities for storage rings, and that means we are able to keep coming up with new ideas,” says Knobloch. *red/arö*



Superconducting niobium cavities are required to generate an electron beam of extremely high stability and quality.

ROUGH OPTICS, SMOOTH SURFACE

A YOUNG INVESTIGATOR GROUP AT HZB HAS PATENTED A **NANOSTRUCTURE FOR SOLAR CELLS**.

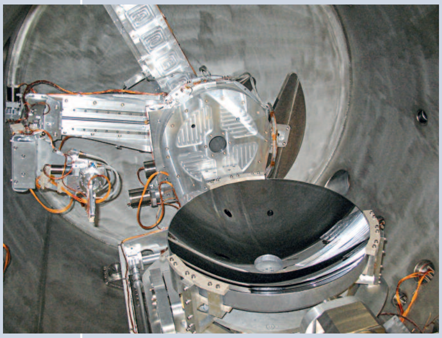


The nanostructure for capturing light is imprinted on silicon oxide (blue) and then "levelled" with titanium oxide (green). The result is an optically rough but physically smooth layer on which crystalline silicon can be grown.

Thin-film solar cells made of crystalline silicon are inexpensive and achieve efficiencies of a good 14 per cent. However, they could do even better if their shiny surfaces reflected less light. “It is not enough simply to bring more light into the cell,” says Prof. Christiane Becker. Such surface structures can even ultimately reduce the efficiency by impairing the electronic properties of the material. The solution that David Eisenhauer worked out as part of his doctorate in Becker's team sounds quite simple, but requires a completely new approach: to produce a substrate that behaves “optically rough” and scatters the light, but at the same time provides a “smooth” surface on which the silicon layer (the most important layer of the solar cell) can grow with virtually no defects.

The procedure involves several steps: first, the researchers imprint an optimised nanostructure onto a silicon oxide precursor layer while it is still liquid and then cure it with UV light and heat. This creates tiny, regularly arranged cylindrical elevations that are ideal for capturing light. However, the absorbing layer of crystalline silicon cannot grow flawlessly on this rough surface, so these structures have an unfavourable effect on the quality of the solar cell. In order to resolve this conflict, a very thin layer of titanium oxide is spin-coated on top of the nanostructure in order to produce a relatively smooth surface onto which the actual absorber material can be deposited and crystallised. This coating has the descriptive name “SMART” for smooth anti-reflective three-dimensional texture. It reduces reflections and brings more light into the absorbing layer without impairing its electronic properties.

20 YEARS OF METROLOGY FOR EUV LITHOGRAPHY IN THE PTB LAB



The EUV reflectometer by PTB with a prototype collector mirror for a pulsed laser plasma EUV light source.

The miniaturisation of microelectronics requires continuous shrinking of the wavelengths used in EUV lithography to achieve the expected resolutions. In response to this demand, Carl Zeiss SMT, the manufacturer of lenses for the lithography machines used by Dutch company ASML, therefore began a collaboration with the German National Metrology Institute PTB in 1998 to develop lenses for the wavelength range used in EUV (wavelengths of a mere 13.5 nm instead of 193 nm, deep UV). For its contribution, PTB used its world-leading radiometric measuring apparatus to determine the optical properties of these mirrors at the working wavelength. PTB is continually expanding its metrological services for semiconductor applications beyond lithography, and is working in the scope of EU H2020 projects together with partners from European industry on the development of EUV and soft-ray-based metrology for nanostructures on wafers. *Frank Scholz/PTB*

NEW BODY OF STANDARDS FOR ENERGY TECHNOLOGIES

Representatives of the Wuppertal Institute have submitted a multi-volume report on energy technologies to the Federal Ministry of Economics and Energy (BMWi). For the project, which was funded by the BMWi, the Wuppertal Institute united the expertise of twelve research institutions. Prof. Rutger Schlatmann, Director of the HZB institute PVcomB, and Dr. Björn Rau were heavily involved in the photovoltaics part of the report. The report gives a comprehensive overview of the innovative and commercial potential of individual PV technologies, evaluates risks and opportunities and the contribution towards achieving the energy turnaround, and examines the need for research and development.

ERC STARTING GRANT AWARDED TO DR. ABATE

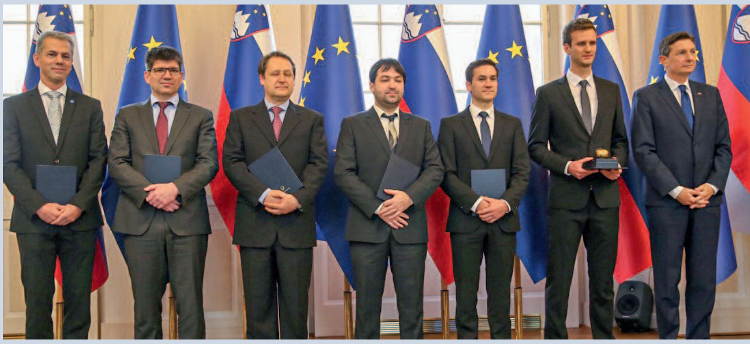
THE HZB SCIENTIST WILL BE SUPPORTED FOR HIS RESEARCH PROJECT ON **PEROVSKITE SOLAR CELLS**.

Antonio Abate is an internationally renowned perovskite researcher.

The ERC Starting Grant supports outstanding researchers in an early phase of their scientific careers with up to 1.5 million euros over five years and is considered one of the most important European awards. Since 2017, Dr. Antonio Abate heads a Helmholtz Young Investigator Group for organometallic perovskite solar cells at HZB. He was a member of Prof. Henry Snaith's team at the University of Oxford when they achieved a stepwise efficiency increase to eleven per cent. Since then, perovskite solar cells have achieved efficiencies in excess of twenty per cent. Abate intends to use the ERC Starting Grant to develop perovskite layers in which the environmentally harmful lead atoms can be replaced by less problematic elements.

"APPLE OF INSPIRATION" FOR HZB SCIENTISTS

MARKO JOŠT, STEVE ALBRECHT AND BERND RECH RECEIVED THIS AWARD FROM THE SLOVENIAN PRESIDENT.



Left to right: Marko Topic, Bernd Rech, Janez Krc, Benjamin Lipovsek, Steve Albrecht, Marko Jost with Slovenian President Borut Pahor.

The "Apple of Inspiration" is an honour bestowed by the Presidential Palace normally to citizens of Slovenia only. It honours achievements in culture, science, sport and society. The Berlin scientists Dr. Marko Jošt, Prof. Steve Albrecht and Prof. Bernd Rech are the first foreigners to receive the prize together with colleagues from the University of Ljubljana. The teams from Ljubljana and Berlin were honoured for their long-standing collaboration, which has led to milestones in the development of perovskite solar cells. The excellent international cooperation not only inspires young scientists in Slovenia, but also contributes to further a strengthening of research into alternative energy sources, according to the Slovenian government.

IMPORTANT APPOINTMENTS

Prof. Marcus Bär, Head of the HZB "Boundary Design" department, is a professor of X-ray spectroscopy at Friedrich-Alexander-Universität Erlangen-Nürnberg. The chair was established in cooperation with Forschungszentrum Jülich in order to reinforce the Helmholtz Institute Erlangen-Nürnberg for Renewable Energy (HI ERN).

Prof. Andrea Denker was appointed by Beuth University of Applied Sciences Berlin and HZB to the joint professorship "Accelerator Physics for Medicine". Since 2006, the physicist has headed HZB's "Proton Therapy" department, which operates the accelerator for eye tumour therapy.

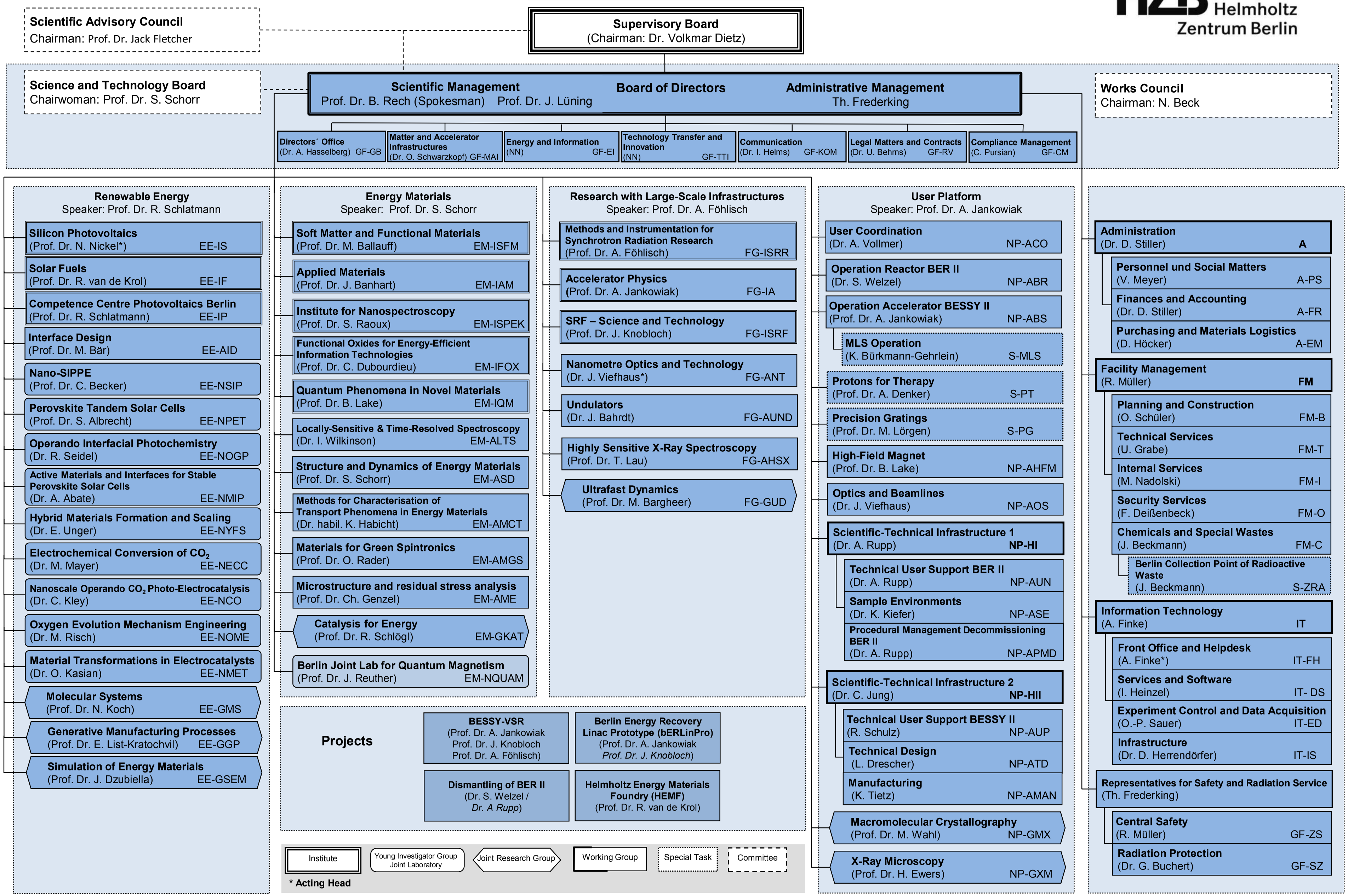
Prof. Thorsten Kamps, head of a workgroup at the Institute for Accelerator Physics, was appointed by Humboldt-Universität zu Berlin and HZB to the professorship "Accelerator-Physics – Generation and Characterisation of High-Brightness Electron Beams".

Prof. Tobias Lau accepted an extraordinary professorship for "Tailored Material Properties – Cluster and Synchrotron Spectroscopy" at the Albert-Ludwigs-University of Freiburg. This joint appointment allows him to research as a department head at HZB and to teach at the University of Freiburg.

Prof. Atoosa Meseck was appointed by Johannes Gutenberg University Mainz and HZB to the joint professorship of "Accelerator Physics – Collective Effects and Nonlinear Beam Dynamics". Meseck researches novel concepts for undulators that are indispensable for generating high-brightness synchrotron radiation.

Organisation Chart HZB

Date June 2019, Rev. 06 June 2019 GB



Site map
The Lise-Meitner-Campus with the research neutron source BER II is located at the HZB Berlin-Wannsee site, whereas the Wilhelm-Conrad-Röntgen-Campus with the electron storage ring BESSY II is located at the HZB Berlin-Adlershof site.

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