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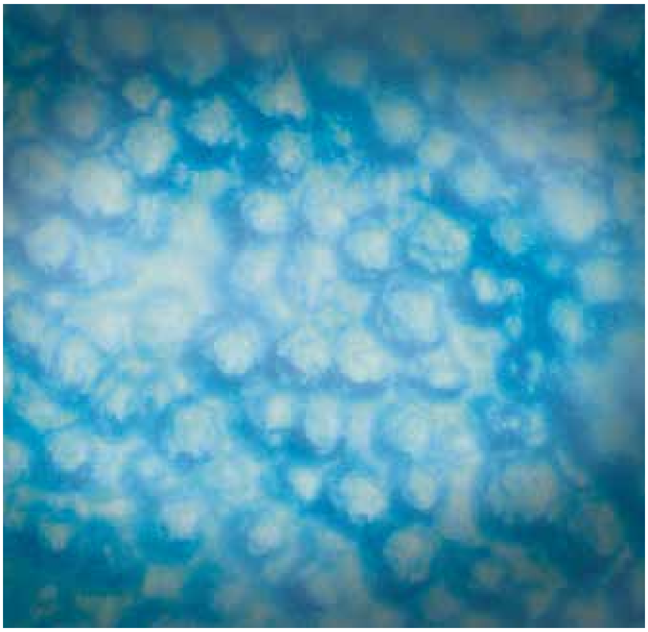
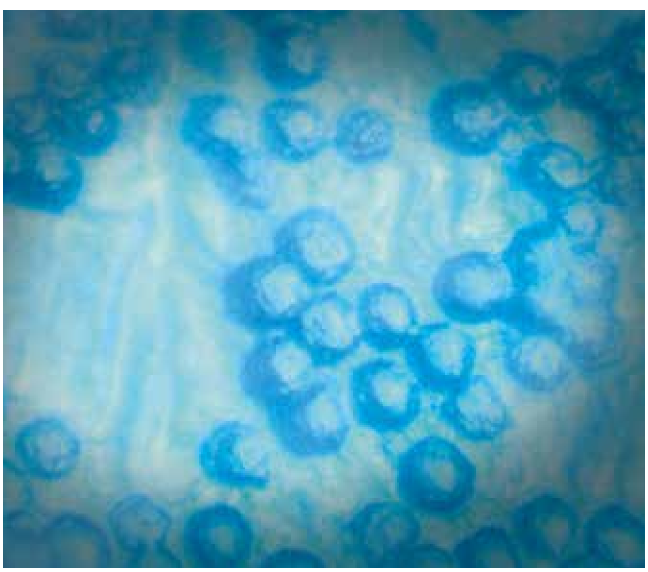
Light Touch: Guiding Algae to Do Delicate Construction Work

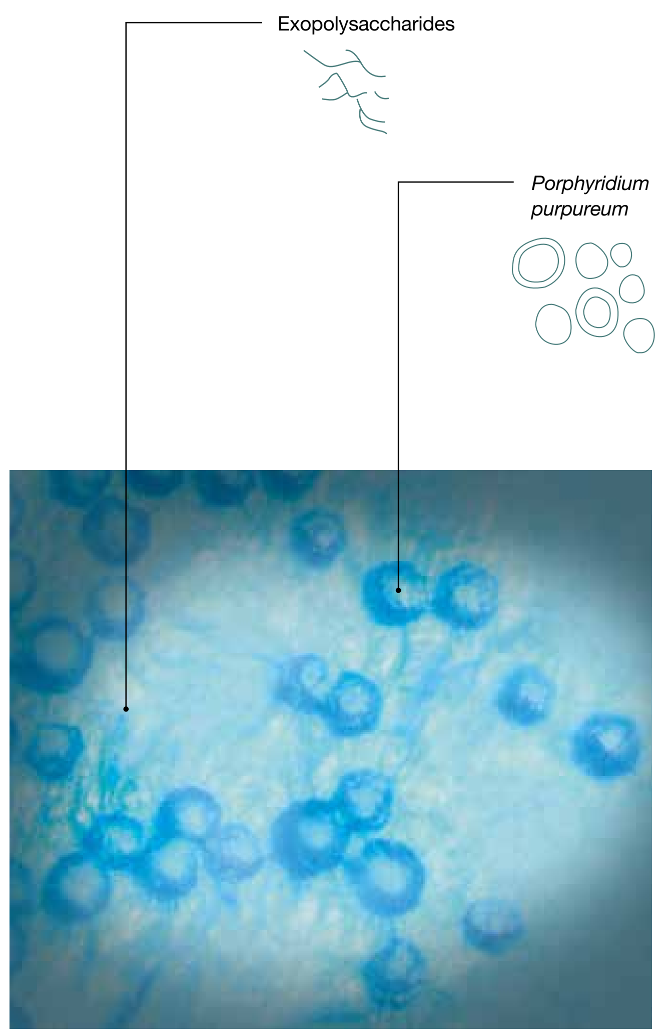
It sounds a bit like magic: Cordt Zollfrank and his team at the Straubing Center of Science (WZS) are using holograms to get microalgae to produce custom-made templates for functional ceramics. This innovative method holds huge potential for applications in technology and biomedicine. For chemists, it is also a long-held dream come true – the prospect of self-structuring materials in 3-D. In recognition of his general research into biogenic polymers at TUM, Zollfrank has been awarded a prestigious Reinhart Koselleck project grant by the German Research Foundation (DFG)

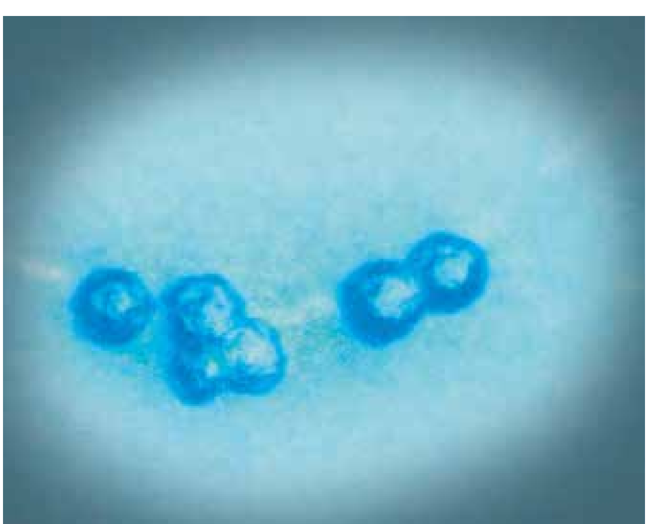
Graphics: ediundsepp / Picture credit: lassedesignen (fotolia.com)

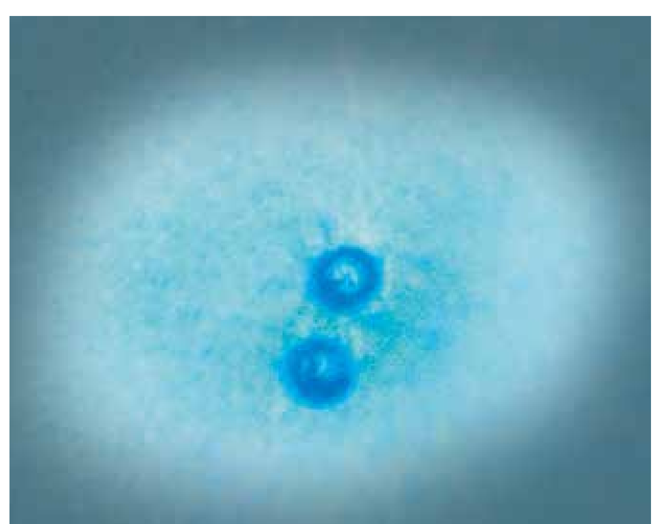


Tiny colonies of the red microalga *Porphyridium purpureum* surrounded by exopolysaccharides (EPS). These are excreted by the red algae during phototaxis, i.e. when they are moving towards the light. The resulting 3-D EPS structures serve as a template for the subsequent conversion into inorganic materials









Picture credits: TUM

Baumeister Licht: filigrane Algenkonstruktionen

Prof. Cordt Zollfrank und sein Team entwickeln am Wissenschaftszentrum Straubing (WZS) ein Verfahren, in dem die Forscher mit Hologrammen Mikroalgen dazu bringen, maßgeschneiderte Schablonen für Funktionskeramiken zu produzieren. Der innovative Ansatz verspricht großes Potenzial für Anwendungen in Technik und Biomedizin. Nebenbei erfüllt sich ein alter Chemikertraum: Material berührungsfrei in drei Dimensionen zu strukturieren. Für seine Grundlagenforschung erhielt Zollfrank mit seinem Fachgebiet Biogene Polymere der Technischen Universität München (TUM) von der Deutschen Forschungsgemeinschaft (DFG) eines der renommierten Reinhart Koselleck-Projekte.

Bioinspirierte holografische Materialsynthese

Die Forscher machen sich zwei Eigenschaften der Purpuralge zunutze: Der Photosynthese betreibende Mikroorganismus bewegt sich stets in Richtung des Lichts und sondert dabei Vielfachzuckerstrukturen ab. Die von der Alge hinterlassene dünne Makromolekülstruktur dient als Matrix, die über chemische Prozesse in Keramik umgewandelt werden kann. Die Vision des Projekts: Setzt man entsprechende Lichtreize, können mithilfe der Algen Werkstoffe in beliebig vielen Formen maßgeschneidert werden. Das Potenzial zur Erzeugung komplex strukturierter Materialien für bestimmte Einsatzgebiete ist enorm: von Elektroden für Batterien über Bestandteile von Spezialfiltern in der Wasserreinhaltung und neue Bildschirm- und Displaytechnologien bis hin zu Knochen- und Gewebeersatz. Wegen ihrer Formenvielfalt und ihrer Fähigkeit zum Selbstaufbau bezeichnet Zollfrank Polysaccharide als den idealen nachwachsenden Rohstoff für keramisches Funktionsmaterial. *Karsten Werth*

Bioinspired material synthesis using holograms – how would you even come up with the idea? "Our research area is biopolymers – or, to be more precise, the production, processing and properties of bioplastics," explains Professor Cordt Zollfrank. "We develop ceramic materials with new structures and functions. Conventional production methods limit the assembly options for ceramics, so generating finer structures calls for an innovative, bioinspired approach."

As a chemist and a forestry and materials scientist, Zollfrank has been working with biological materials for quite some time. After taking up his professorship at TUM in October 2011, he continued developing his concept of synthesizing materials using holograms and was able to convince the DFG to fund this new approach as part of its Reinhart Koselleck project program. Zollfrank is keen to emphasize that, alongside the innovative concept and his own track record, the excellent research infrastructure at the Straubing Center of Science was a key success factor in securing the funding. Here, six Bavarian universities cooperate within a TUM-led center of excellence for renewable resources, benefiting from excellent links with business and politics. The various labs work closely together and actively foster interdisciplinary exchange.

Over the next five years, 1.25 million euros will be available to fund a research group working on this visionary project. "This level of backing for higher-risk endeavors is very rare in the German research landscape," underscores the 45-year-old researcher. "We are enjoying a high level of freedom here." Alongside Zollfrank, "we" so far refers particularly to Daniel Van Opdenbosch, who recently completed his doctorate with distinction under Zollfrank's supervision and is now setting up the new research group.

Inspired by nature

The field of biogenic polymers is – literally – all about natural science. Researchers work with any natural substance composed of biological macromolecules (biopolymers) – cellulose, polysaccharides, and collagen – and use them to develop bioplastics. In some cases, these have already been commercially adopted, one example being the wood-plastic composites now widespread in the construction sector as a replacement for tropical timber in outdoor decking. Biodegradable compounds are also available on the market, used for instance in plant pots made of elephant grass (miscanthus), which break down in the ground after the plants take root. But the TUM researchers are taking all this a giant step further. One of their focus areas is biotemplating – the transfer of biological structures to inorganic materials. By way of illustration, Zollfrank places a piece of rattan on his office table. The cross-section of this palm cane, extremely popular with furniture makers, reveals its porous structure – which offers astonishing possibilities. To start with, the rattan is heated in an inert atmosphere and converted into wood charcoal. A ceramic material is generated from this by infiltrating the carbon bodies with silicon heated to over 1400 degrees Celsius. This triggers the formation of silicon carbide, a heat-resistant substance that has also featured in the black protective tiles on space shuttles. In terms of the substance itself, this laboratory-generated ceramic is now far removed from rattan. But the new material completely mimics the rattan's structure, albeit in slightly contracted form. The reward for all this effort lies in the detail, as Zollfrank reveals: "This method enables us to produce ceramics from naturally occurring, micron-sized structures. Silicon carbide is the second-hardest material in existence after diamond. You can't even drill holes in that, no matter how small."

Ceramic pine cones

The researchers are investigating both the structure and functionality of biogenic materials. Pine cones are one of the objects of interest here, and specifically the way they open and close in response to the surrounding air humidity. The interesting objective is that this motion is not due to cell metabolism but solely to material properties. The researchers are keen to gain an understanding of this type of process, allowing them to generate synthetic materials with similar functionality. One such example might be blinds on office windows that open and close themselves depending on the sun's rays, without the need ▷

Picture credit: Bauer

Researchers from the field of biogenic polymers examine the quality of miscanthus (elephant grass). Besides its interest to applied archaeologists, miscanthus is also a valuable source of biomass. Working closely with local farmers (Martin Soetz, Pfatter) who grow this grass, researchers are busy exploring its full application potential

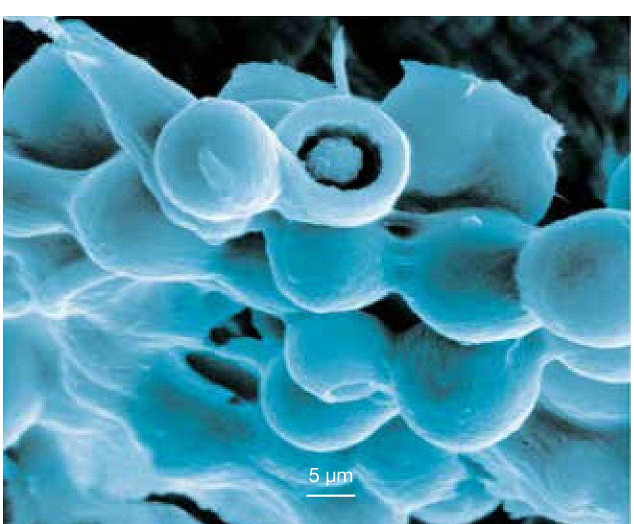
Taking advantage of highly efficient, natural microstructures: One focus area of Zollfrank's group is biotemplating, a method for the transfer of biological structures into inorganic materials. Here, researchers are inspecting wood samples for biotemplating. The process yields a ceramic with hierarchical, nanometer-precision replication of the wood's structure

Picture credit: Bauer

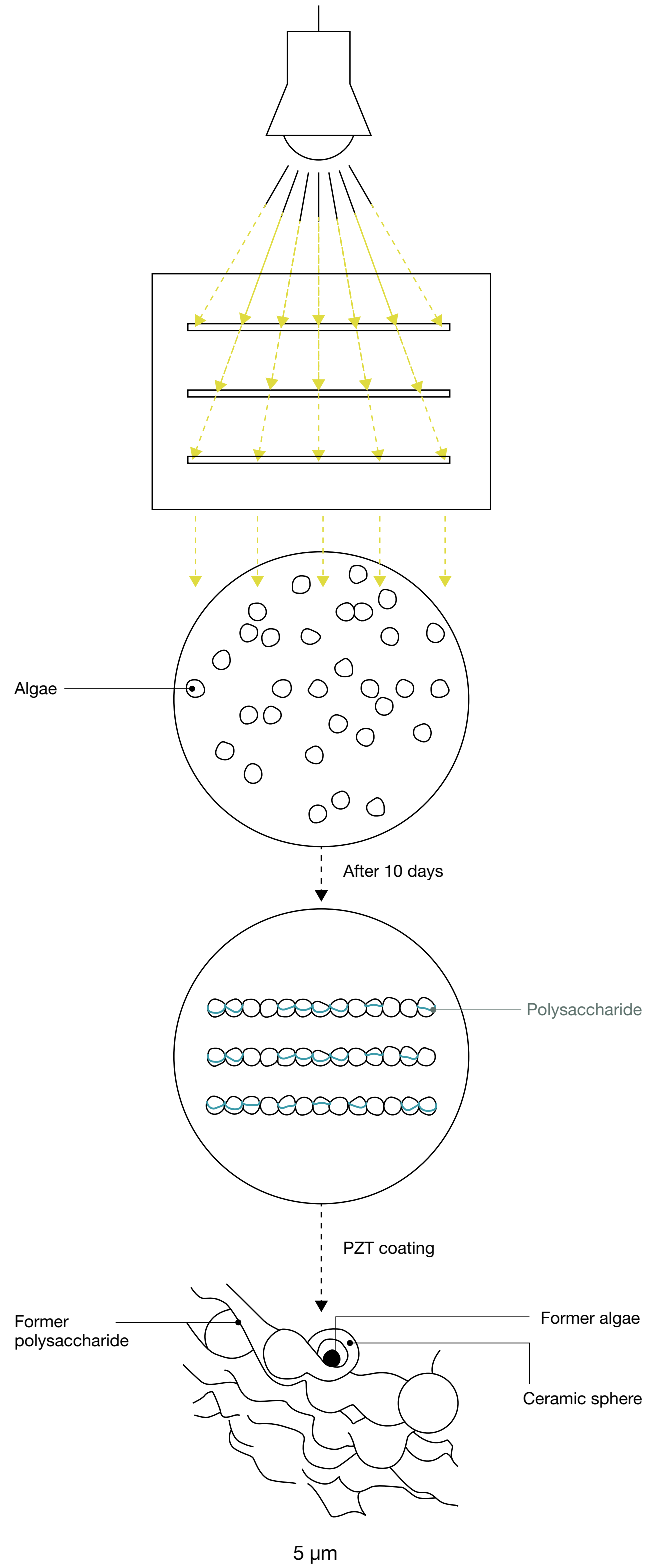
for electric operation. However, Zollfrank is careful not to raise undue expectations: “We still have a long way to go until we’ll really be able to build inorganic actuators.” Still, the foundations have already been laid: it transpires that, when the pine cone is converted into ceramic, not only the macrostructures in the wood, but even the nanoscale structures related to the microfibrils in the cell walls can be retained in the inorganic material. Summing up the main thrust of his research, Zollfrank declares: “We are looking to learn from nature as we work out what functional and design principles would be most useful for new materials. It is fascinating to take biological properties such as adaptation, self-organization, self-healing and energy autonomy and transfer them to ceramics.”

Harnessing phototaxis

The red microalga *Porphyridium purpureum* plays a key role in this new Reinhart-Koselleck project, granted funding in November 2013. The WZS researchers are exploiting two properties of these algae. Being photosynthetic microorganisms, they always move toward the light (phototaxis), and they secrete exopolysaccharides in the process. The fine macromolecular structures left behind during algal phototaxis serve as a matrix that could be transformed into ceramic, for instance. The vision shared by Zollfrank and Van Opdenbosch is that, if they can manage to manipulate the microalgae to produce one single template, they can probably adjust them to create any number of customized forms by applying the appropriate light stimuli. The researchers had already taken an important step prior to the DFG’s backing by using chemical processes to coat the microalgae with lead zirconium titanate (PZT), a piezoelectric ceramic. If these formations are heated to temperatures of 500 to 600 degrees Celsius, all organic matter is eliminated and what remains are hollow ceramic ▷



Picture credit: TUM/Graphics: ediundsepp (Source: TUM)



Finest structures created by algae: Light guides the growth of red microalgae, which secrete polysaccharides during the process. The researchers have managed to coat these structures with lead zirconium titanate (PZT), a piezoelectric ceramic. The formations are then heated to 500-600°C to eliminate all organic matter. The result is a structure made of hollow ceramic spheres

spheres. The next step was to solve the challenge of how to construct two-dimensional models from polymers. They accomplished this via an experiment that involves shining light through a mask into a Petri dish inoculated with the microalgae. After a certain amount of time, the microalgae align themselves with the pattern of the penetrating light.
Looking ahead, Van Opdenbosch explains: “The last, critical question is whether we will manage to construct a three-dimensional framework from polysaccharides – will phototactic structuring with microalgae succeed?” The plan devised by the researchers for bioinspired holographic synthesis is intended to work like this: A laser beam is directed at an object through a mask. This object reflects the light, and the superimposed object beam and reference beam form a hologram. A substrate with a microalgae suspension is placed in the immediate proximity of this three-dimensional light structure. The microalgae should then align themselves with the edges of the hologram and grow along them. After a few days, the culture medium is removed, and what remains should be the polymer structure secreted by the microalgae as they move – a ready-made template for conversion into inorganic material. Adding suitable reactants such as silicic acid or calcium compounds then produces a new substance. “Both the structure of the hologram and the choice of reacting agents for chemical conversion can be varied, so we hope to gain ceramic materials with a wide range of forms and functions,” says Van Opdenbosch. The potential for generating materials with complex structures for specific applications is huge: from electrodes for batteries and components for special water purification filters to new screen and display technologies, and bone and tissue replacements. Their variety of forms and ability to self-assemble leads Zollfrank to describe polysaccharides as the ideal renewable feedstock for functional ceramic materials. As the most common naturally occurring biopolymer, the cellulose they consist of is readily available, and large-scale industrial capacity to process cellulose products is already a given. That, then, is the vision. There are certainly still several issues to resolve – for instance, how the polysaccharide structure produced by the microalgae is to remain stable. The field of biogenic polymers is entering new territory in materials synthesis by generating three-dimensional structures directly from microorganisms. “We are harnessing a real biological principle to synthesize new materials – and there are very few examples of that in research to date,” confirms Zollfrank.

Baking without a mold

A major advantage of biotemplating over other methods of producing materials – such as 3-D printing – is that it enables synthesis of extremely fine structures. The process based on microalgae takes this to an unbeatable new level. Single algal cells are approximately five micrometers in size. The polysaccharide strands they secrete are significantly smaller still, at around a hundred nanometers across, so that we need an electron microscope to see them. This is the scale at which the scientists are building 3-D structures – and solely by means of specific light patterns. A dream come true for chemists, who have long sought ways to produce self-structuring 3-D materials without contact. “It’s like baking without a mold,” concludes Zollfrank. The current project is still in the early stages: equipping the lab, determining the number of participating colleagues and developing an interdisciplinary network for collaboration between biologists, chemists, materials scientists and physicists. Whether the vision will ultimately become reality is not yet clear. “But one thing is certain,” emphasizes Zollfrank: “We’ll learn a great deal along the way. Not just about material synthesis itself, but also about the mechanisms of phototaxis and the use of optical devices.” *Karsten Werth*

As a chemist and a forestry and materials scientist, Professor Cordt Zollfrank appreciates the excellent research infrastructure at the Straubing Center of Science, where six Bavarian universities cooperate in the field of renewable resources research

Picture credit: Bauer