Das Freiburger Zentrum für interaktive Werkstoffe und bioinspirierte Technologien
Freiburg Center for Interactive Materials and Bioinspired Technologies

FIT

Report 2023

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REPORT

2023

FIT

FREIBURG CENTER FOR INTERACTIVE MATERIALS AND BIOINSPIRED TECHNOLOGIES

FIT

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University of Freiburg

Georges-Köhler-Allee 105

79110 Freiburg

Germany

P: (+49) 761 203 67879

F: (+49) 761 203 4709

E: mail@fit.uni-freiburg.de

I: http://www.fit.uni-freiburg.de

Secretariat: Christian Neumann

Info Management: Manuel Birk, Holger Frey

Managing Director: Prof. Dr. Jürgen Rühe

Administrative Management: Dr. Stefanie Meisen

Scientific Coordination: Dr. Olga Speck

Cover photos:

Top: Exterior view of the *liv*MatS Biomimetic Shell @ FIT. © ICD/ITKE/IntCDC University of Stuttgart, Photo: Conné van d'Grachten

Bottom: Inside view of the livMatS Biomimetic Shell @ FIT. Press conference with (f.l.t.r.) Prof. Dr. Jan Knippers, Prof. Achim Menges (University of Stuttgart), Rektorin Prof. Dr. Kerstin Krieglstein, Prof. Dr. Jürgen Rühe, Prof. Dr. Thomas Speck (University of Freiburg). © FIT Universität Freiburg, Photo: Dr. Olga Speck

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Table of Contents

FOREWORD

FIT INTO THE FUTURE

The year 2023 was, so to speak, year 1 AC (After Corona) and most events could be held in person again. These include the colloquia, which are now taking place regularly again, and the opportunity to welcome guest researchers back to the FIT. Zoom and ChatGPT are simply a very poor substitute for fruitful scientific discourse. Personal contacts are particularly important for an activity as trans- and interdisciplinary as the FIT.

The past year was once again packed with attractive materials research at the FIT, as this annual report shows. A particular highlight in 2023 was certainly the opening of the *liv*MatS Biomimetic Shell. In July, we celebrated the grand opening of a 200 m² pavilion right next to the FIT building, which sets standards in many respects as a pioneering architectural project for a modern urban society. The building is the result of a long-standing and very fruitful cooperation between the Cluster of Excellence for Architecture, IntCDC, the University of Stuttgart and *liv*MatS. The architects and civil engineers from Stuttgart and the scientists from Freiburg are working together actively and creatively in the field of bio-inspired materials research with the aim of developing biomimetic, sustainable and adaptive components for buildings. The building is constructed using a very resource-efficient timber frame construction technique inspired by the sea urchin skeleton and is characterized by features such as the use of recycled concrete, a construction design based on climate and acoustics simulations, robot-assisted component generation and robot-assisted building construction. A special highlight is the autonomous shading of the building, which is inspired by the way pine cones work. When the interior heats up too much, 3D-printed building elements shade the windows with the help of humidity-controlled actuation. When the indoor temperature returns to normal, they open again to let in sunlight - and they do so completely autonomously without the use of electrical energy, driven solely by the warmth of the sunlight. As a flagship project for sustainable construction, the pavilion has attracted a lot of attention for the University of Freiburg. The interested groups came from Germany and abroad and ranged from experts to the general public and politicians. Pictures and further information on this exciting project can be found on the cover page and in the corresponding articles inside this FIT annual report.

With the aim of introducing young students to future-oriented research during their Master's degree, the *liv*MatS and IPROM research clusters once again organized the MasterLab. Over 70 students have now successfully taken part in the program, which demonstrates its great appeal. The program includes a mixture of participation in cutting-edge research challenges and the teaching of core competencies ('soft skills') that are important for scientific work. The program has met with an extremely positive response and represents an important building block in introducing young talents to research at FIT.

The cooperation in the field of materials research with our sister institute, the "Living Materials Convergence Center" (LIMC2) at Penn State, has also developed very satisfactorily. In addition to new seed grants, 7 students accompanied by 2 faculty members visited *liv*MatS/FIT this summer for a period of 8 weeks to gain their first research experience. They worked as part of the IPrism project, which deals with the generation of large-volume, interactive infrastructure and is funded by the American research organization NSF on the basis of a joint German-American proposal. The project was a great success with both the American participants and the supervisors, as can be seen from the fact that there were more than 130 applications for a further 6-7 places for the 2024 round.

It is a good and established practice that the foreword to the annual report provides an opportunity to say thank you - thank you to all the good souls whose work in the background enables us to conduct outstanding science. Without their constant commitment, we would not be able to produce internationally competitive scientific work. Special thanks go to the

administrative and technical staff for their constant commitment, which has enabled us to keep the "ship afloat" and everything running smoothly despite the notoriously tight staffing levels. We would also like to thank our scientific advisory board for their helpful advice and tips. As every year, they traveled to Freiburg to advise us on many strategic issues. The external perspective on our activities and measures is always very helpful for us.

FIT thrives in particular on the creativity and enthusiasm of the many young scientific staff and our established FIT members. It is always a pleasure to observe the scientific curiosity and commitment of our young co-workers. The acquisition of attractive new projects and the implementation of exciting research projects are the lifeblood of FIT and constantly drive it forward. Last but not least, we would like to thank our many supporters and sponsors inside and outside the university, whose contributions make many things at FIT possible in the first place.

In the coming year, we at FIT will continue to tackle the task of making as significant a contribution as possible to the positive development of society through future-oriented and sustainable materials research with energy and confidence. I hope you enjoy reading our annual report.

Jürgen Rühe

(Executive Director FIT)

THE CENTER

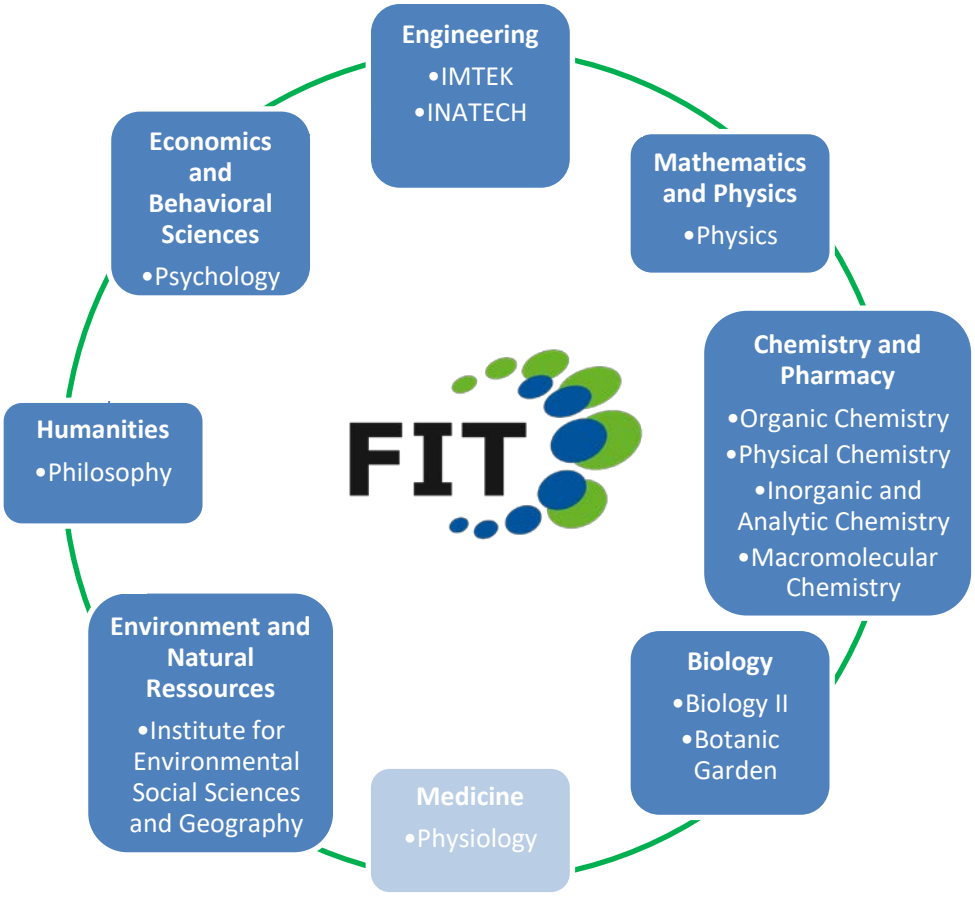
STRUCTURE

The FIT is a research institution of national and international importance for the development of future-oriented, innovative materials and materials systems. Special focus is placed on materials systems that react to changes in the environment and thus, inspired by plants and animals, have life-like functions. Following the model of living nature, these "vital" materials systems are interactive, adaptive, energy-autonomous, self-repairing, self-improving or even learning. These extraordinary properties and functions make them a decisive advance in the sustainable development of technology and society.

FUTURE FIELDS

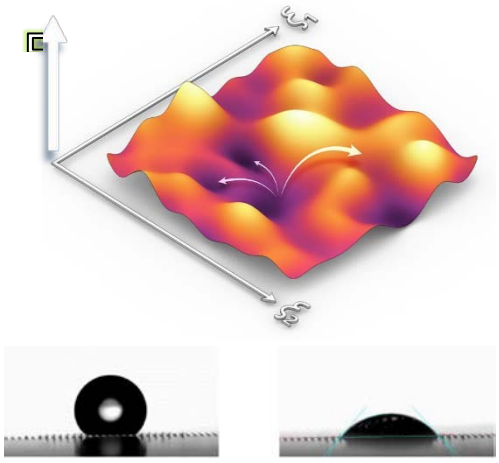
Adaptive and Active Polymer Materials

Today's technical materials and materials systems are designed in such a way that they have more or less constant properties. These properties are given to them during the manufacturing process and should (apart from a little aging) not change in the course of time in the desired application. This immutability of material properties constitutes accordingly one of the core concepts of modern engineering and a rational systems design. In nature, on the other side, all living beings are designed to adapt as good as possible to their environment and to react to changes in environmental conditions with an appropriate response. A (young) sunflower, for example, moves its head according to the position of the sun in order to capture as much sunlight as possible, while a pine cone opens and closes depending on the ambient humidity to release its seeds under favorable conditions. Indeed one might rephrase Darwin’s description of evolution by “Survival of the most adaptive”.



Overview of the various faculties and institutes that carry out disciplinary and interdisciplinary projects within the framework of basic research at FIT. A list of current and completed projects is available on the FIT website.

The aim of the research program in the Future Field “Adaptive and Active Polymer Materials” is to develop new types of technical materials and advanced systems that do not have unchanging properties, but react to changing environmental conditions by adapting their shape and structure. This requires the generation of complex responsive systems, where the system can end up in different states depending on the nature of the stimulus, so that it can adapt to changes in the environment in a similar way as it is the case for living things. Fig. 1 gives an artist’s impression for an energy landscape of such a multi-stimulus responsive system. Depending on the strength or type of the stimulus the system can end up in very different states represented by valleys in the energy landscape. This simplest case is observed, when the system responds to the stimulus only while the stimulus is still present. Such a behavior of the system is commonly called responsive. A simple example for responsive behavior is thermal expansion of a material. Switching, on the other side, occurs when the stimulus leads to reversible movement of the system between two states (example: photoisomerization of azo compounds). Here the system remains (at least for a while) in the second state and can return back to the original one through application of a different stimulus. Truly adaptive materials, however, can store these structural changes and retain the properties changed this way for further, later use. Taking the picture described above true adaptivity is only achieved when the stimulus leads to a reshaping of the energy landscape and thus keeps a memory of the conditions to which it had been exposed to. This way it resembles in a way a simple form of training / learning.



Artists impression of an energy landscape describing the effect of several stimuli acting on a materials system b) Wetting of a water drop on a mechanically actuated sample © Rajak, Rühe; unpublished results

Examples for such adaptive changes of materials, in which the outer appearance of the system is altered, are an origami-like folding of structures or the actuation of hair-like surface structures. But also the inner structure of a material can adapt to external stimuli as it is the case for auxetic materials which stiffen as a reaction to the application of a certain force. This adaptability of materials can be used to adjust properties of materials such as adhesion, wettability (see Fig. 1b) or mechanical properties, to environmental changes and thus opens up novel design spaces for the generation of complex objects. Materials systems with adaptive properties will allow breakthrough innovations in many different fields such as soft robotics, smart optical devices, self-adaptive medical prostheses and orthoses, adaptive safety equipment, adaptive light guiding systems or interactive architectural components such as façade elements, which open and close with changes in the weather conditions.

In more complex systems not only one stimulus directs the behavior of a materials system, but usually several different stimuli act together, either subsequently or simultaneously. In this case the different signals need to be processed (and eventually weighed against each other). This weighing of different system responses leads to a gated behavior, not unlike logic gates in computer science (AND, OR, NOT). For example, systems can be designed which actuate in a certain fashion when either sufficient heat or humidity are present (OR condition). In another case bilayers systems can be generated where for example high humidity is required to “unlock” the system. An example could be here a lowering the glass transition temperature of a hydrogel layer rendering the layer much softer. This softening effect could then allow thermal or magnetic actuation of the bilayer system, where the movement is otherwise “frozen in”. Such a system requires for a successful actuation the presence of both stimuli, a typical AND condition. From a more general point of view, pathways to reach such complex adaptive behavior, which show features of an embodied intelligence, are the generation of reaction networks or the creation of complex metamaterials.

In nature, which serves as a great source of inspiration for the envisioned interactive and adaptive materials, the creation of such systems involves the integration of structures across many size scales, e.g., from the chemical structure of a cellulose molecule to the overall structure of a many meters high bamboo. Only when the components on the various length scales for cell to tissue and whole organism interact with each other in an appropriate way, adaptive behavior is observed. This is in a similar way true for artificial systems, where molecular changes e.g. by photoisomerization or swelling lead to macroscopic changes of an actuator.

However, the spatial domain is not the only one which needs to be addressed, but also timing can be crucial. In cases when the response to the signal relaxes with time (i.e. the system returns spontaneously, without the presence of an external stimulus back to the original state) also the time difference between the receptions of two separate stimuli will play an important role on the systems behavior. An example is a situation, where the first stimulus is needed to unlock the system and allow a response of the system to the second one. When relaxation after the first is faster than the application of the second stimulus, the “memory” of the occurrence of the

first stimulus will be erased, the system remains locked and the presence of the second stimulus yields no systems response. However, when the arrival of the second stimulus, is faster than relaxation, the system is unlocked and can respond to this stimulus. Accordingly, complex adaptive systems might also require the consideration of different time scales ranging from rapid molecular changes, such as the closing or breaking of chemical bonds occurring within nano- to microseconds, to very slow processes such as thermal relaxation or creeping of materials that might take minutes or days. Successful development of interactive and adaptive materials thus requires a scale-bridging approach both from a theoretical and experimental point of view that extends all the way from a molecular oriented scale in time and space to that of a macroscopic object.

Jürgen Rühe

Biomimetic, Biobased and Bioactive Materials Systems

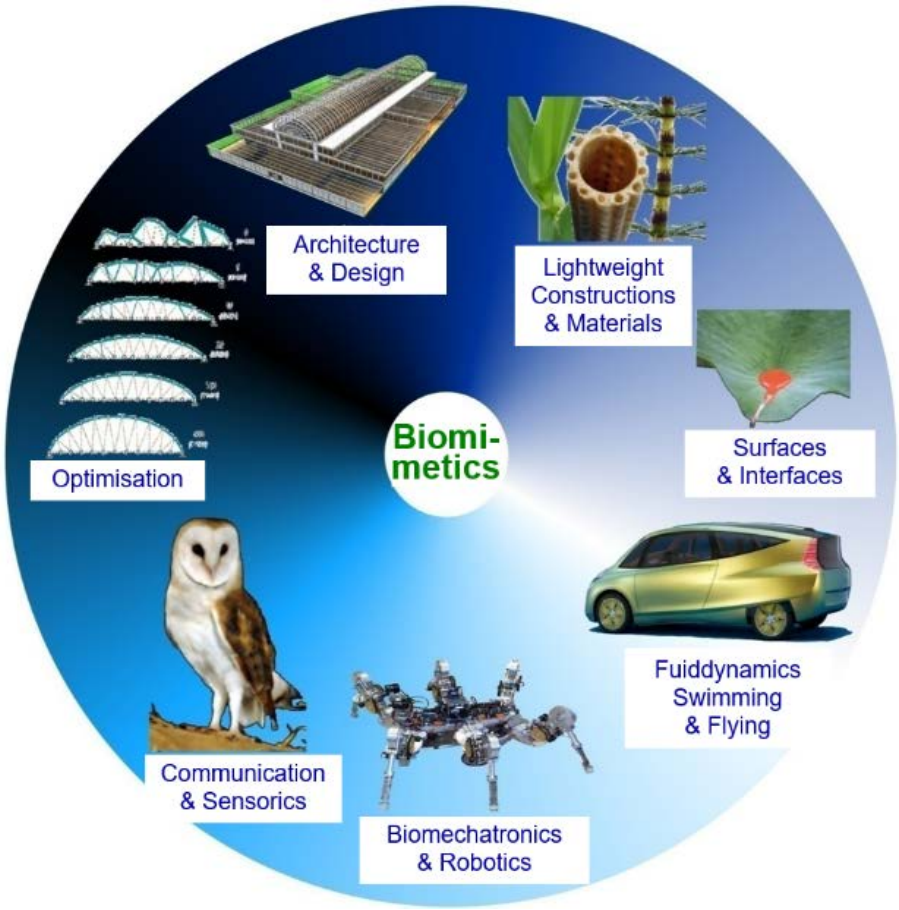


Fig. 1: Various fields of biomimetic research. © Plant Biomechanics Group Freiburg

In this future field the research focus lays on the development and construction of bioinspired, biomimetic, biobased and bioactive material systems. FIT projects cover the first two thirds of the value chain from basic research analyzing the biological role models and developing new materials systems to the production of functional demonstrators in lab bench dimensions. In addition to the transfer

of functional principles from living nature to technical systems, this also includes the development of new active hybrids by the integration of synthetic and biological components, and the bioactive functionalization of materials and (micro)systems to enable them to interact with proteins, cells and tissues.

Biomimetic materials systems @ FIT

During the last decades biomimetics has attracted increasing attention as well from basic and applied research as from various fields of industry and building construction. Biomimetics has a high innovation potential and offers the possibility for the development of sustainable technical products and production chains. The huge number of organisms with the specific structures and functions they have developed during evolution in adaptation to differing environments represents the basis for all biomimetic R&D-projects. Novel sophisticated methods for quantitatively analyzing and simulating the form-structure-function-relation on various hierarchical levels, which is possible due to the various testing devices present at the FIT, allow new fascination insights in multiscale mechanics and other functions of biological materials and surfaces. Additionally, new production methods enable for the first time the transfer of many outstanding properties of the biological role models into innovative biomimetic products for reasonable costs (Fig. 1). In the FIT we concentrate on the development of biomimetic materials systems with various self-x-properties including self-repair, self-adaptation, self-cleaning and self-organization. Other research topics deal with bioinspired materials systems with pronounced energy dissipation, trainable materials systems, and the usage and development of 3D- and 4D-printing technologies for the production of novel bioinspired materials systems. Examples are plant inspired soft robots and soft machines and self-adaptive motile technical systems inspired by plant movements. For the latter especially hyromorphs, as e.g. Pine cones and scales (Fig. 2), are of increasing interest.

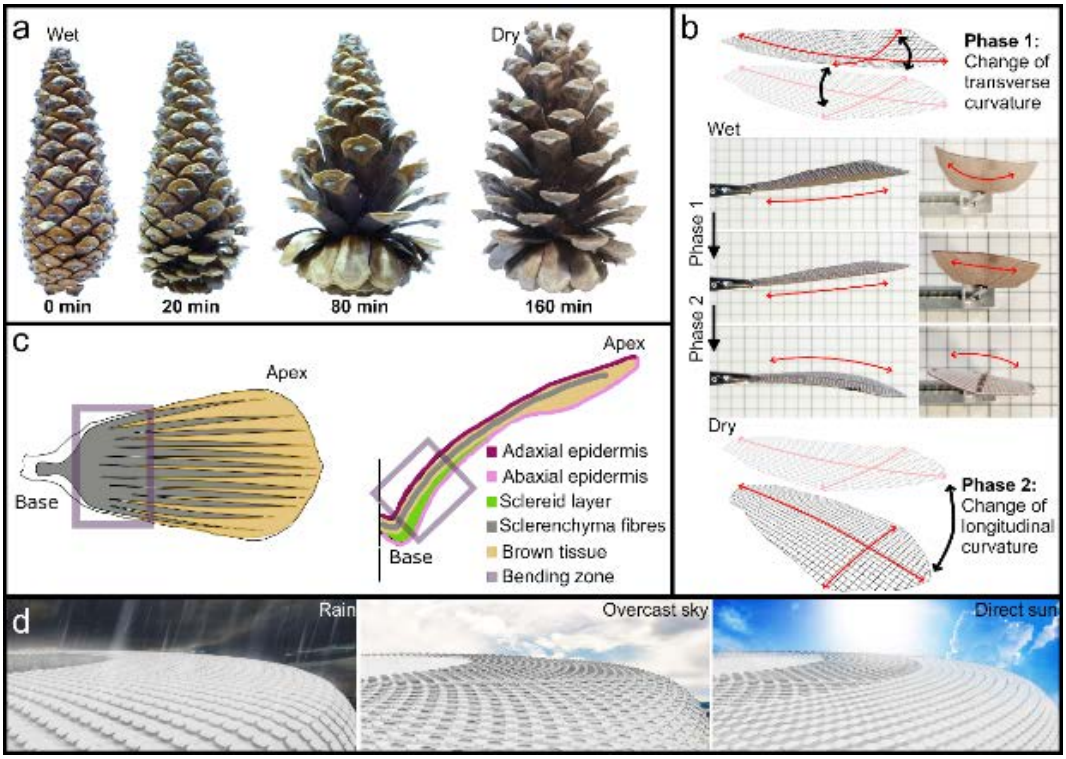


Fig. 2: Pine cone actuation, functional morphology and biomimetic self-sufficient compliant hygromorpic systems. (a) A pine cone shows sequential seed scale movements during the drying-induced opening sequence. (b) Multi-phase motion of a 4D-printed scale structure consisting of copolymer strands with embedded cellulose fibrils as the actuating layer and ABS polymer strands as the resistance layer. (c) Schematic top view (left) and longitudinal section (right) of a pine cone scale. (d) Vision of a modular smart-building skin consisting of shingle-like structures exhibiting tropistic behaviour for sun-tracking and nastic behaviour for fast hull closure upon an increase of environmental humidity. Figure from [1].

The reasons for this interest are, that they: (1) harvest energy from the environment (no energy consumption), (2) are sensor, actuator, reactive movable element and support structure in one materials system, (3) show high level of structural and functional integration, and (4) display extraordinary high functional resilience and robustnesss [1].

Biobased materials @ FIT

In the biobased materials research @ FIT, we try to use biomimetic approaches to design novel materials from renewable resources. Our efforts particularly focus on the utilization of lignocellulosic biopolymers towards the design of advanced structural load carrying materials and materials systems, and of actuating materials for soft machines. One such project has attempted to develop novel processing approaches of lignin, the second most abundant biopolymer on earth, by utilizing a liquid crystalline cellulosic polymer as processing aid and lubricant. This processing approach is inspired by the biosynthesis and the morphogenesis of the plant cell wall. During the plant cell wall morphogenesis, a liquid crystalline cellulose / hemicellulose network serves as a host structure for the in-situ polymerization of monolignols. to finally deliver a high-strength, high toughness composite lignocellulosic material. The resulting lignocellulosic blends can be processed in solution by direct ink writing, which paves the way to new processing avenues for lignocellulosic polymers and thus novel applications.

In the framework of the Cluster of Excellence Living, Adaptive and Energy-autonomous Materials Systems (*liv*MatS), which is located at the FIT, in 2021 the “*liv*MatS Pavilion" was built in the Botanic Garden of the University of Freiburg as a model for a bioinspired sustainable construction. After the end of the Covid19 restrictions we started in 2022 to use very successfully the “*liv*MatS Pavilion” for activities in our outreach project “Learning from Nature in Nature”. The “*liv*MatS Pavilion” is inspired by the saguaro cactus (*Carnegia gigantea*) and the prickly pear cactus (*Opuntia* sp.), which are characterized by their special reticulated light-weight wood structure. Based on this bioinspiration civil engineers and architects of Cluster of Excellence “Integrative Computational Design and Construction for Architecture” (IntCDC) at the University of Stuttgart realized the “*liv*MatS Pavilion by using computer-aided design methods and robot-controlled production. The "*liv*MatS Pavilion" represents a prime example for a bioinspired sustainable construction with a light-weight biobased supporting structure [2,3].

Fig. 3: Exterior of the *liv*MatS Biomimetic Shell @ FIT. © ICD/ITKE/IntCDC University of Stuttgart, Photo: Conné van d'Grachten

***liv*MatS Biomimetic Shell @ FIT**

In the summer of 2023, a second bio-inspired research pavilion was completed next to the FIT building. The *liv*MatS Biomimetic Shell @ FIT is designed according to biomimetic principles and is the result of a close collaboration between the Clusters of Excellence Integrative Computational Design and Construction for Architecture (IntCDC) at the University of Stuttgart and Living, Adaptive and Energy-autonomous Materials Systems (*liv*MatS) at the University of Freiburg (Fig. 3, 4).

In this joint project, the researchers have built a lightweight timber pavilion in which they are testing and researching new materials and construction methods. Over the next years, it will be used as a research pavilion to test materials systems and energy harvesting devices developed in *liv*MatS and in the FIT under realistic outdoor conditions. For the construction of the "*liv*MatS Biomimetic Shell @ FIT", the Stuttgart architects used new computer-based planning methods, robotic manufacturing and construction processes, and new forms of human-machine interaction, which enable significant resource savings compared to conven-

tional timber construction. The modular structure and design is based on the structure of the sea urchin skeleton. It consists of individually arranged panels, making the *liv*MatS Biomimetic Shell @ FIT particularly light and strong.

Fig. 4: Interior of the *liv*MatS Biomimetic Shell @ FIT showing the solar gate weather-sensitive shading system. © ICD/ITKE/IntCDC University of Stuttgart, Photo: Conné van d'Grachten

Researchers from the two clusters worked closely together to develop the "solar gate", a weather-sensitive shading system made of bio-based, 4D-printed materials (Fig. 4, 5). Mounted in a skylight, it regulates the building's climate by shielding the interior from sunlight and high heat loads on hot summer days and letting in sunlight in winter and on cloudy summer days. The 'solar gate', which passively adapts to solar conditions, is based on a biomimetic principle inspired by pine cones, which open and close in a humidity-controlled manner [4].

Fig. 5: Solar gate weather-sensitive shading system. © ICD/ITKE/IntCDC University of Stuttgart, Photo: Conné van d'Grachten

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Thomas Speck

(Micro)Systems for Energy Conversion, Storage and Energy-autonomy

In this future field, the research focuses on the development and construction of material systems for energy conversion and storage. As such, inspired by nature, materials and systems are developed for the conversion of solar energy (solar cells and photoelectrochemical cells for artificial photosynthesis), chemical energy (fuel cells), thermal energy (thermoelectric generators) and vibrational energy (triboelectric generators). One aspect thereby aims to realize material systems with an embedded energy autonomy, i.e. materials systems which are ideally able to harvest the required energy from the ambient. In that sense, the materials and systems developed in this future field range from macro to highly embedded micro systems. As most ambient energy forms are intermittent, systems for energy storage must also be developed, so that the required energy is available on demand. Breaking with classical modular approaches, one vision is hereby to develop multifunctional conversion and storage systems at the highest

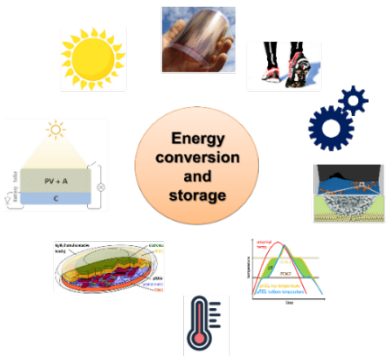
level of integration, realizing a seamless integration of both functions. In this context, advanced multifunctional material processing techniques are of highest importance to realize this integration challenge.

Material systems for energy conversion and storage @ FIT

The largest activities in the future field are presently associated with the research activities in research area A of the livMatS Cluster in which novel concepts and systems for energy autonomous materials systems are developed.

Solar energy conversion and storage

Solar energy is converted and stored as electrical charges in SolStore devices; devices, which fuse the function of light-induced charge carrier generation/separation and charge carrier storage at different levels of integrations, ranging from 3 electrode systems, in which a solar cell shares an electrode with an electrochemical energy storing system (supercapacitor or battery) to 2 electrode systems, in which the light-induced charge carrier generation/ separation and charge carrier storage are truly embedded in one multifunctional material system.



Different forms of energy conversion and storage and associated materials and systems. © Area A of the *liv*MatS Cluster.

This central *liv*MatS research is complemented by other FIT research projects in the future field related amongst others to a) solar energy conversion with novel tandem solar cells or photoanodes for photoelectrochemical water splitting, b) electrochemical energy conversion with bioinspired materials for Pt-free fuel cells as well as c) improved electrochemical energy storage with novel battery concepts and materials and interfaces.

Thermal energy conversion and storage

This area is anticipated by the development of highly efficient thermoelectric generators (TEGs) with integrated phase shift materials to be used as a storage unit for thermal energy. The corresponding project ThermoBatS is therefore again aiming at an intricate fusion of energy conversion and storage. The thermoelectric materials chosen are fabricated as highly nano-micro scale powders and formulated as thermoelectric inks or pastes. Fabrication of TEGs happens via dispensing or printing into flexible substrate materials, thus creating a versatile multi-material system suitable for the ambient temperature range. Other projects outside of livMatS will tackle the area of high-temperature energy harvesting using powder-pressed and sintered or electroplated thermoelectric materials. A third direction to be followed in all projects is the characterization of thermoelectric materials and systems.

Mechanical energy conversion

In *liv*MatS, triboelectric generators are the actual main topic of research in the project TriboGen. Here, we will do an extensive study on the fundamental physical effects of triboelectric charge generation, to gain more insight into this phenomenon, which is known for thousands of years but still a matter of scientific debate. As a result, optimized materials and suitable surface topologies will be developed for highly efficient triboelectric generators. Charge extraction will happen through innovative concepts and automatic frequency tuning will be performed through the mechanical design of self-adaptive triboelectric vibration harvesters.

These named projects are exemplary for the trend of energy research followed in FIT. Aside of the mentioned activities additional related projects are planned to widen the research platform with additional and highly innovative concepts for energy conversion, storage and transfer.

Anna Fischer & Peter Woias

New Materials: Societal challenges

Andrea Kiesel[1,2], Lore Hühn[1,3], Oliver Müller[1,3], Olga Speck[1], Rainer Grießhammer[1], Martin Möller[1], Julius Fenn[2], Philipp Höfele[1,4]

[1]Cluster of Excellence livMatS @ FIT – Freiburg Center for Interactive Materials and Bioinspired Technologies; [2]Department of Psychology, University of Freiburg; [3]Department of Philosophy, University of Freiburg; [4]Institute of Philosophy, Freie Universität Berlin, Germany

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Technological advance promises to solve major problems. For example, in the context of new materials systems the development of sustainable, long-living materials systems that harvest energy from the environment might contribute to reduce human impact on climate change. Yet, technological advance challenges society and this challenge increases the faster and broader the technological advance is. On the one hand, technological advance is considered sceptical due to concerns that depend on the perception of risks and benefits as well as ethical concerns and trust in technologies per se. On the other hand, promises of technological advance are often misunderstood or misinterpreted. In the context of biomimetics, humans tend to believe that bio-inspired novel technologies are per se more sustainable, yet nature or to be more precise biological evolution is not goal-oriented and biomimetic products are not automatically sustainable[1].

Identifying and addressing the societal challenges of novel technologies requires interdisciplinary and transdisciplinary collaboration [2]. In this Future Field, philosophers, psychologists and sustainability researchers work together with material scientists (from several disciplines like chemistry, physics, engineering) and biologists to describe and characterice novel materials systems and identify their potential use as well as eventual risks and benefits. Novel tools are developed to assess and evaluate these materials systems and resulting novel technologies both from an empirical point of view in terms of societal acceptance [3] as well as from an analytical point of view in terms of sustainable development including aspect re-cycling [4]. Further, important concepts like "nature" and "life" are considered in the current discourse to increase inter- and transdisciplinary understanding and to identify misconceptions and narratives [5]. Feeding back the results helps material scientists to understand societal concerns and misconceptions and sustainability considerations and hopefully contribute to increase acceptance for the scientific approaches and novel technologies.

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Andrea Kiesel

CORE FACILITIES

Imaging of Materials Systems

- Scientific head: Prof. Dr. Anna Fischer[1,2,3]
- Responsible manager and scientist: Dr. Y. Thomann[1], Dr. R. Thomann[1,2,4] and Dr. E. Balaghi[1,2,3]

[1]Freiburg Center for Interactive Materials and Bioinspired Technologies (FIT), University of Freiburg, Georges-Köhler-Allee 105, 79110 Freiburg, Germany; [2]Freiburg Materials Research Center (FMF), University of Freiburg, Stefan-Meier-Straße 21, 79104 Freiburg, Germany; [3]Institute of Inorganic and Analytical Chemistry (IAAC), Inorganic Functional Materials and Nanomaterials, University of Freiburg, Albertstraße 21, 79104 Freiburg, Germany; [4]Institut für Makromolekulare Chemie, Albert-Ludwigs-Universität Freiburg, Stefan-Meier-Straße 31, 79104 Freiburg, Germany

The Core Facility “Imaging of Materials System” (CF1@FIT) is a specialized laboratory equipped with several electron microscopes (200 kV HR-TEM/STEM, 120 kV TEM, SEM, FIB/SEM), two atomic force microscopes (AFM), a µ-CT, and a variety of peripheral devices.

The facility is generally open to all research groups within the university as long as their projects are funded on a non-profit basis. Users can perform their own measurements after training or can have their samples analyzed by CF1 staff. Beside instrumental training, the Core Facility provides expertise in 3D digital imaging, EDX spectroscopy and electron diffraction analysis, and sample preparation for specific applications.

The main focus of CF1 is multi-length scale 2D and 3D microscopy based on the variety of tools available in the specialized laboratory (Fig.1).

For more information about the types of devices and contact persons, one can visit: https://miap.eu/miap-unit/core-facility-imaging-of-materials-systems/.

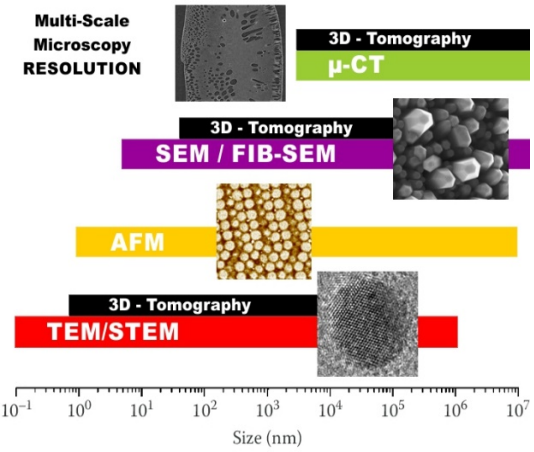

Fig. 1: CF1 - Multiscale, Various microscopes and Deeper insights. Image © Y&R Thomann

Fig. 2 and 3 show two exemplary results generated at CF1 over the past year. One shows a FIB/SEM cross-sectional image of a microelectrode-cavity array, the other a 3D TEM tomography of a mesoporous carbon particle coated with a polymer shell.

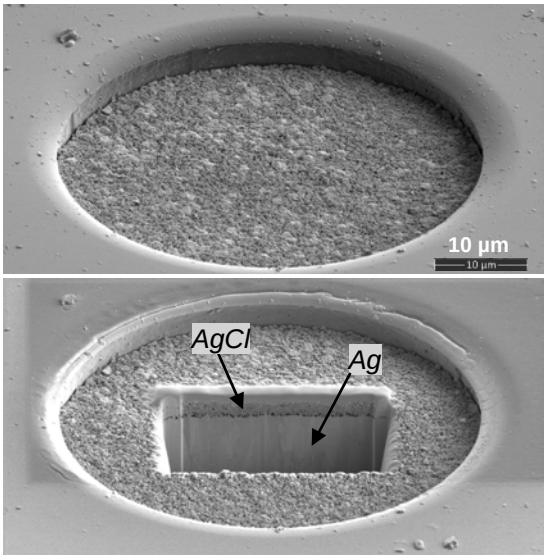

Fig. 2: FIB/SEM cross-sectional imaging of a micropatterned Ag/AgCl microelectrode-cavity-array, a sensor which is used in a mini electronic device for electrophysiological measurements. (sample: T. Ensslen / group Prof. Behrends, Membrane Physiology, University Freiburg). Image © Y. Thomann

Over 20 papers with CF1 contributions have been published in 2023. Examples of these, including pictures and videos, are available at the following link and in the references cited at the end of the contribution.
https://zenodo.org/communities/cf1

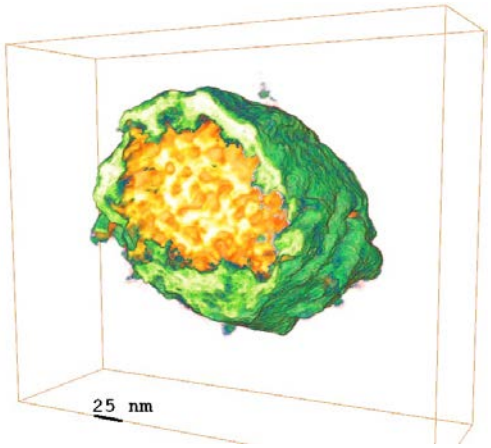

Fig. 3: TEM tomography of a nanoparticle with a mesoporous carbon core (orange) and a polymer shell (green). The internal structure of the particle is revealed by virtual sectioning of the particle in Avizo® software. (sample: N. Ortlieb / group Prof. A. Fischer) Image © R. Thomann

One of CF1's ongoing research foci involves the development and application of an in-situ electrochemical (scanning) transmission electron microscopy method, abbreviated as in-situ EC (S)TEM. Fig. 4 illustrates the application of this in-situ method to study the electrodeposition of zinc nanostructures. This work is performed by Dr. Esmael Balaghi within the Momentum grant of Prof. Dr. Anna Fischer funded by the VolkswagenSftiftung.

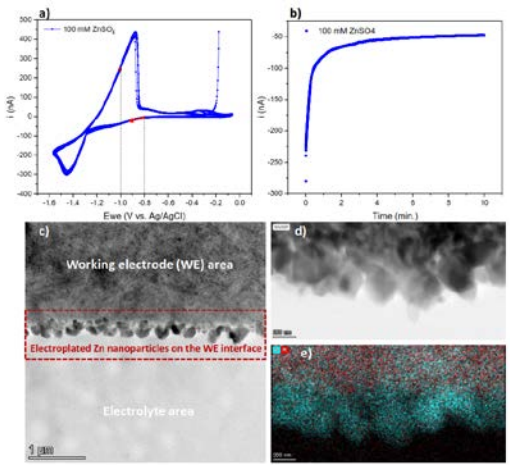

Fig. 4: a) Cyclic voltammogram of a 100 mM $ZnSO_4$ solution in our in-situ electrochemical liquid (S)TEM cell (electrolyte flow rate = 10 µl.min^{-1}; voltage scan rate: 50 mV.s^{-1}). b) Chronoamperometry results showing Zn electrodeposition from a 100 mM $ZnSO_4$ solution in our in-situ electrochemical liquid (S)TEM cell (electrolyte flow rate = 10 µl.min^{-1}; applied voltage: -1.4 V vs. Ag/AgCl). c) TEM image of the working electrode interface during Zn electrodeposition (100 mM $ZnSO_4$). d) HAADF-STEM image and e) HAADF-STEM-EDX analysis of the working electrode interface during Zn electrodeposition (100 mM $ZnSO_4$).

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Functional Processing

Manufacturing technique for bioinspired materials with focus on nanolithography, film technology, and generative processes

- Scientific head: Prof. Dr. Claas Müller[1,2]
- Responsible manager: Dr. Jing Becker[1]

[1]FIT Core Facility "Functional Processing",
[2]IMTEK Department of Microsystem Engineering, Laboratory for Process Technology

Short description of research goals: Manufacturing technique for bioinspired materials with focus on nanolithography, macromolecular foil technology, and 3D-printing technology

In order to support the research projects running in FIT, a powerful technology department, Core Facility "Functional Processing", is established for functional design and efficient manufacturing of (micro-) systems and adaptive bioinspired materials.

The Core Facility "Functional Processing" concentrates particularly on the fabrication of nano- and micro-structures on macromolecu-

lar foils. Besides UV-NIL (UV-nanoimprint-lithography) as well as HE-NIL (hot-embossing-nanoimprint-lithography) technologies, various novel manufacturing technologies, such as roll lamination, thin film deposition, surface modification, aerosol jet printing technology, electrophoretic deposition, as well as screen printing technology are developed for special applications on polymer foils.

The equipment installed in the Core Facility "Functional Processing" is divided into two different categories according to the operation complexity. The category 1 includes the Cryomill system for material grinding with its integrated liquid nitrogen cooling system, the Stork roll laminator and the electrophoretic deposition system (EPD) from Permatecs. For this equipment category, after the application from the users and the evaluation by Core Facility "Functional Processing" group, the applicants would receive a clearly defined training course offered by the CF 2 stuffs. Following the training activities, the applicants will be issued a permit to work on the system.

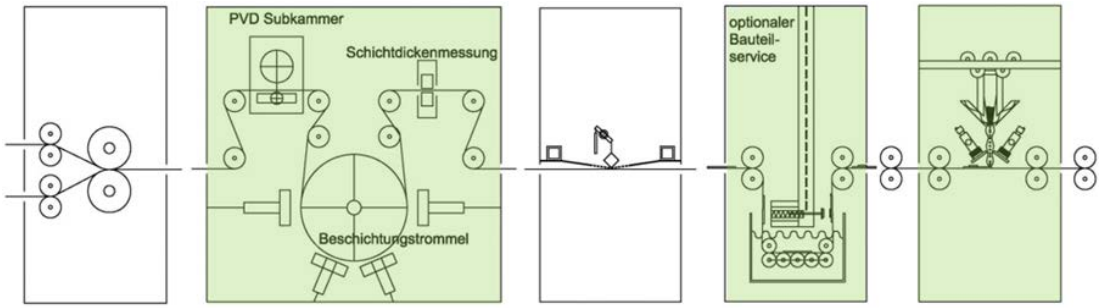

Fig. 1: Arrangement of the process modules in the technology platform 2 (from left): roll laminator, PVD & PECVD system, screen printer, electrophoretic deposition system and aerosol jet printer. © Core Facility 2, FIT, Freiburg

For the other system in CF 2, due to the operation complexity and the maintenance requirements, the users outside the CF 2 group are not allowed to perform alone on the systems. The equipment in this category could only be operated by the CF 2 stuffs.

In year 2023, Core Facility “Functional Processing” has cooperated with research group Speck in Fit on the topic of “Plant-inspired humidity-driven bending actuator”. It belongs to the livMatS booster project in the project area C (Longevity and Demonstrators) and project area B (Adaptivity and Demonstrators). The goal of this booster project is to develop a bio-inspired smart bilayer system with reversible and programmable actuation functionalities, which is activated by the variation of relative humidity (hydraulic movement) in the surrounding environment. The bending curvature of the actuator depends on the ambient relative humidity, the mechanical properties and the dimension of the monolayers, the arrangement of the individual layers, and the preparation procedure. The functional principle of bi-layers will be applied to transform the dimensional change in individual layers into a system bending activity.

In year 2023, a DFG research project applications have been submitted. These planned research projects is listed below:

DFG research project “*µBlue- Micro fuel cell accumulators and charging concepts for environmentally friendly energy storage systems*” (under review)

The concrete goal of the project is the development of a self-sufficient micro fuel cell accumulator (µBZA) including optimized charging and operating electronics. This µBZA is intended as a long-term vision in conjunction with an energy harvester to reliably supply autonomous sensor and actuator systems with energy. The centerpiece is a µBZA with integrated hydrogen storage as an environmentally friendly energy converter. The proton-conducting membrane of the µBZA is applied directly to the hydrogen storage unit, which makes active components such as pumps or

pressure regulators superfluous. With the hydrogen stored in the storage tank and the oxygen from the ambient air, the stored chemical energy is directly converted into electrical energy. The only waste products are heat and water, which can be reused to recharge the storage.

To achieve the largest possible electrochemically active surface area, the interface between the PEM and the catalyst layer must be maximized. This will be achieved by well-defined nano- or micro-patterns patterned by nanoimprint lithography. This nanostructured interface increases the "three-phase region" between reactant, catalyst and electrolyte. In this case, the performance of µBZA should be significantly improved compared to conventional fuel cells with a "flat" membrane. In this case, it would be possible to adapt the output power of the µBZA to the performance data required for an application through targeted nanostructuring of the PEM-catalyst interface.

By extending a micro fuel cell with an electrolyze and charging electronics, the primary element "fuel cell" becomes a secondary element "fuel cell accumulator". The µBZA system does not require any environmentally harmful materials and at the same time has higher energy densities than commercial miniaturized battery systems.

Publications

1. Sizi Hu, Haochen Wang, Max D. Mylo, Jing Becker, Bo Cao, Claas Müller, Christoph Eberl, Kaiyang Yin, “Programmable Multimaterials Silicone Hopper”, Advanced Functional Materials (submitted).

2. Emre Firat Özel, 2, Dennis Pede, Claas Müller, Yi Thomann, Ralf Thomann, Hadi Mozaffari-Jovein, “Microstructure of Selective Laser Melted 316L Under Non-equilibrium Solidification Conditions”, Journal of Experimental and Theoretical Analyses (submitted).

Modelling and Simulation of Materials Systems

- Scientific head:
  Prof. Dr. Michael Moseler[1,2,3]
- Responsible manager:
  PD Dr. Michael Walter[2,1,3]

[1]Fraunhofer IWM, MikroTribologie Centrum µTC, Karlsruhe; 2FIT – Freiburg Center for Interactive Materials and Bioinspired Technologies [3]Cluster of Excellence *liv*MatS @ FIT, [4]Institute of Physics, University of Freiburg

Short description of research goals: Concept Development, Modeling and Simulation of Interactive Materials Systems.

Understanding of the complexity of materials systems is based on simplification. We create a simplified version of reality for which we derive our expectations based on laws that can be first principles or more empirical. Generally, these laws are formulated as mathematical equations. These are derived from surprisingly few basic relations like the Maxwell- or the Schrödinger equations on the fundamental level, but gain complexity through the vast number of par-ticles involved in real life materials.

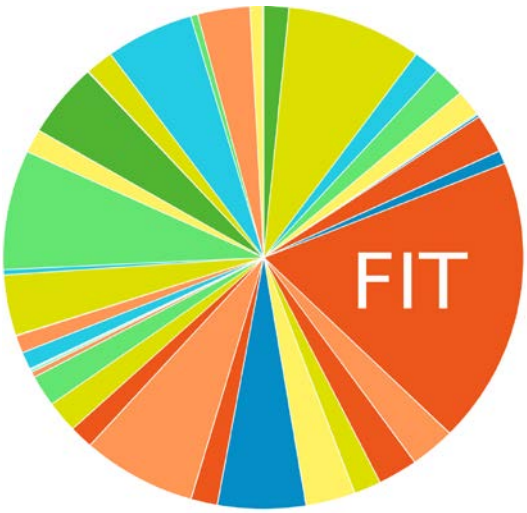

Fig. 1: Partition of computational time used on the full NEMO-cluster in the year 2023. The fraction used by FIT/CF3 is highlighted and amounts to 17%. (© RZ University of Freiburg)

As there are are only a few problems that can be solved analytically, numerical treatment of the problems is in order. Here, the ever increasing available computational power becomes beneficial. The funding granted by the Landesstiftung and the German Research Foundation was therfore used in 2017 for an extension of the NEMO-cluster located at the Rechenzentrum of the University of Freiburg. The cluster provides 18.000 cores in total and is accessible by research groups within Baden-Württemberg. The FIT participates in the within the “shareholder” principle providing preferential access, where the granted funding allowed to contribute to 5.6% of the hardware. The synergy obtained by this strategy was a large gain in computational resources for FIT. The last year’s use of computational resources added up to 17% of the full capacity of NEMO making FIT the top user of the cluster (Fig. 1).

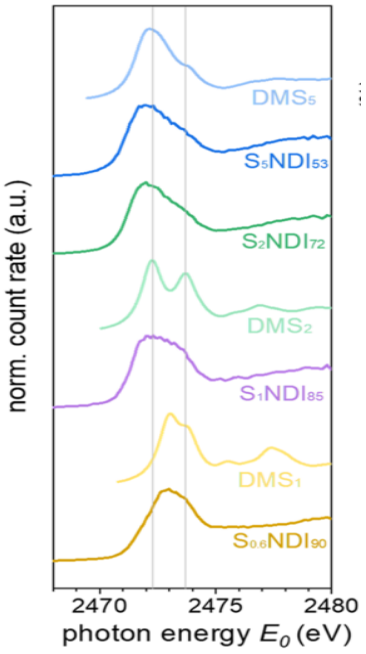

Fig. 2: Comparison of experimental XAS spectra of LiS cathode materials (SxNDIy) and simulated spectra (DMSz) reveals the S-chain length z [3] (© 2023 The Authors. ACS Applied Energy Materials)

The Walter research group is mainly concerned about properties of materials on the molecular scale. These nevertheless also determine macroscopic effects as in lithium-sulfur batteries for example. Here, the calculations provide insights about molecular level phenomena that cannot be achieved by experimental means alone [1-3], Fig. 2. The studies within the CF3 research group resulted in a total of 6 peer reviewed publications in the year 2023. Further investigations are reported in the Highlights.

An example of a successful FIT based collaborations are the studies of carbenes used for CHick chemistry and ongoing work on O_2 release from anthracene-endoperoxides.

On a more basic level of interest for experimental groups, modeling of meso- and macroscopic properties are possible with finite element methods. These allow solving (coupled) differential equations that determine materials and their composites or even complex experimental setups. In this respect the software COMSOL, available through the technical faculty, is an easy to use and versatile tool to model may different general-purpose simulation software based on advanced numerical methods. It allows for fully coupled multiphysics, but also single-physics modeling. An introductory course on the basic usage of this software was provided to the new *liv*MatS PhD students in 2023. Further discussion about COMSOL setups and the supervision of a COMSOL aided Masters Thesis were conducted.

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[2] S. de Kock, K. Skudler, R. Matsidik, M. Sommer, M. Müller, M. Walter “NEXAFS spectra of model sulfide chains: implications for sulfur networks obtained from inverse vulcanization” Phys. Chem. Chem. Phys. 25 (2023) 20395-20404, doi: 10.1039/D3CP02285D

[3] R. Matsidik, K. Skudler, S. de Kock, A. Seifert, M. Müller, M. Walter, S. Choudhury, M. Sommer On the Effect of Sulfur Strand Length on Electrochemical Performance of Dual Redox-Active Sulfur-Naphthalene Diimide Cathode Materials ACS Applied Energy Materials 6 (2023) 9466−9474, doi: 10.1021/acsaem.3c01438

MANAGEMENT

Prof. Dr. Jürgen Rühe
(Managing Director)
IMTEK
Department of Microsystems Engineering
Chemistry and Physics of Interfaces

Prof. Dr. Thomas Speck
(Deputy Managing Director)
Plant Biomechanics Group
Botanic Garden
Faculty of Biology

Dr. Stefanie Meisen
(Administrative Director), FIT

Dr. Olga Speck
(Scientific Coordinator), FIT

DIRECTORATE

The Board of Directors of the FIT consists of five full-time professors from the participating faculties of the University of Freiburg that must also be members of the FIT. These professors are appointed by the Rectorate for a term of three years on the recommendation of the general meeting. The Directorate elects the Managing Director and the Rectorate appoints him for a term of three years. The Board of Directors is responsible for managing the business and decides on all matters that are not assigned to another body of the university. It coordinates the tasks to be performed within the FIT and draws up an annual research and financial plan. The members of the Directorate also include the respective Managing Director of the FMF and a representative of the young scientists. In 2023, members of the Directorate were:

Prof. Dr. Jürgen Rühe
(Managing director)
Faculty of Engineering

Prof. Dr. Thomas Speck
(Deputy managing director)
Faculty of Biology

Prof. Dr. Anna Fischer
Faculty of Chemistry and Pharmacy

Prof. Dr. Peter Woias
Faculty of Engineering

Prof. Dr. Bastian E. Rapp
(Managing director of the FMF)
Faculty of Engineering

Dr. Can Dincer / Dr. Céline Calvino
(Representative of young scientists)
Faculty of Engineering

MEMBERS

Laboratories with the corresponding infrastructure and office space are made available to members for a limited period of time. The members have access to the three Core Facilities. In 2023, the members included (in alphabetical order):

Dr. Juliane Borchert (Faculty of Engineering)

Dr. Céline Calvino (*liv*MatS)

Dr. Can Dincer (Faculty of Engineering)

Prof. Dr. Patrick Dondl (Faculty of Mathematics and Physics)

Prof. Dr. Christoph Eberl (Faculty of Engineering)

apl. Prof. Dr. Christian Elsässer (Faculty of Mathematics and Physics)

Prof. Dr. Anna Fischer (Faculty of Chemistry and Pharmacy)

Prof. Dr. Stefan Glunz (Faculty of Engineering)

Dr. Frank Goldschmidtböing (Faculty of Engineering)

Prof. Dr. Rainer Grießhammer (Faculty of Environment and Natural Resources)

Dr. Dorothea Helmer (Faculty of Engineering)

Prof. Dr. Lore Hühn (Faculty of Humanities)

Prof. Dr. Thorsten Hugel (Faculty of Chemistry and Pharmacy)

Prof. Dr. Henning Jacob Jessen (Faculty of Chemistry and Pharmacy)

Prof. Dr. Andrea Kiesel (Faculty of Economics and Behavioral Sciences)

Dr. Peter Koltay (Faculty of Engineering)

Prof. Dr. Ingo Krossing (Faculty of Chemistry and Pharmacy)

Dr. Tom Masselter (Faculty of Biology)

Prof. Dr. Edoardo Milana (*liv*MatS)

Prof. Dr. Michael Moseler (Faculty of Mathematics and Physics)

Prof. Dr. Claas Müller (Faculty of Engineering)

Dr. Anayancy Osorio (Faculty of Engineering)

Dr. Charalampos Pappas (*liv*MatS)

Prof. Dr. Lars Pastewka (Faculty of Engineering)

Dr. Uwe Pelz (Faculty of Engineering)

Dr. Thomas Pfohl (Faculty of Mathematics and Physics)

Prof. Dr. Bastian E. Rapp (Faculty of Engineering)

Prof. Dr. Günter Reiter (Faculty of Mathematics and Physics)

Prof. Dr. Ralf Reski (Faculty of Biology)

Prof. Dr. Jürgen Rühe (Faculty of Engineering)

Dr. Viacheslav Slesarenko (*liv*MatS)

Dr. Olga Speck (Faculty of Biology)

Prof. Dr. Thomas Speck (Faculty of Biology)

Dr. Severin Vierrath (Faculty of Engineering)

PD Dr. Michael Walter (Faculty of Mathematics and Physics)

Prof. Dr. Peter Woias (Faculty of Engineering)

Dr. Uli Würfel (Faculty of Mathematics and Physics)

Prof. Dr. Roland Zengerle (Faculty of Engineering)

Scientific Advisory Board

The Scientific Advisory Board accompanies the scientific work of the FIT and shall provide the directorate with suggestions for its further development. Members of the Scientific Advisory Board are external university professors whose research focus lies in the field of activity of the FIT. They are appointed by the rectorate for a period of five years. The following professors belonged to the Scientific Advisory Board:

Spokesperson: Dr. Karine Anselme (Institut de Science des Materiaux de Mulhouse (IS2M), France)

Deputy spokesperson: Prof. Dr. Christoph Weder (Adolphe Merkle Institute, Fribourg, Switzerland)

Prof. Dr. Eduard Arzt (Saarland University and Leibniz Institute for New Materials, Germany)

Prof. Dr. Clothilde Boulanger (Université de Lorraine, France)

Prof. Dr. Ingo Burgert (ETH Zurich, Switzerland)

Prof. Dr. Peter Fratzl (Max Planck Institute of Colloids and Interfaces, Potsdam, Germany)

Prof. Dr. Oskar Paris (University of Leoben, Austria)

Prof. Dr. Eric Yeatman, Imperial College London, UK)

Integrative Board

The Integrative Board is set up as a university-internal advisory body and monitors the development of the FIT. It works towards the reconciliation of interests of the faculties and institutions involved in FIT. In 2022 the following persons were members of the Integrative Board, with the deans always changing to the winter semester.

Prof. Dr. Jürgen Rühe (Managing Director of FIT)

Prof. Dr. Thomas Speck (Deputy Managing Director of FIT)

Prof. Dr. Heiner Schanz (Dean of the Faculty of Environmental and Natural Resources)

Prof. Dr. Sonja-Verena Albers (Dean of the Faculty of Biology)

Prof. Dr. Michael Thoss (Dean of the Faculty of Mathematics and Physics)

Prof. Dr. Andreas Bechthold (Dean of the Faculty of Chemistry and Pharmacy)

Prof. Dr. Roland Zengerle (Dean of the Faculty of Engineering)

Prof. Dr. Lutz Hein (Dean of the Faculty of Medicine)

Prof. Dr. Bastian Rapp (Management Director of the Freiburg Materials Center)

Dr. Frank Krüger (Head of Freiburg Research Services)

Dr. Karine Anselme (Spokesperson of the Scientific Advisory Board)

Dr. Stefanie Meisen (Administrative Management of FIT)

Figures and Finances

Unfortunately, it was not possible to keep the number of projects at the same level in 2023. With only 26 projects, excluding the livMatS Cluster of Excellence, the budget could not be maintained at the same level. The livMatS Cluster of Excellence, which is associated with us as a project group and is funded as part of the Excellence Strategy, started its fifth year of funding in 2023. This year, 69 projects, 33 long-term projects, 21 booster projects and 16 associated projects with a total budget of 6 million euros were running within the cluster. Together with livMatS, 8.8 million euros were thus implemented in the FIT.

Of the funds spent, 76% was spent on personnel. A total of 290 employees were active this year, including 46 postdocs, 137 doctoral students, 68 Master's students and 15 Bachelor's students.

In addition to expenditure on personnel, 12% of the budget was spent on material resources and 12% on new investments. To understand the figures, please refer to the following charts and tables for further details.

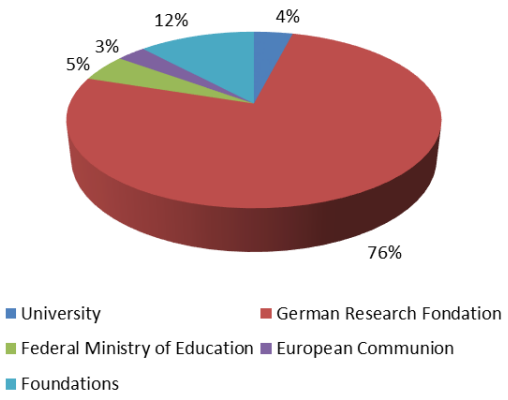

Fig. 1: Percentages participation of the FIT-budget 2023

Tab. 1: Budget from 2020 until today in € (* inclusive livMatS-Cluster)

	2020	2021	2022	2023
German Research Foundation	*6.950.882	*9.529.305	*6.675.231	*6.717.302
State Country BW	98.857	112.471	43.164	0
Federal Ministry of Education	243.345	552.549	562.775	426.420
European Communion	576.875	360.206	286.354	245.600
Foundations	777.965	1.714.111	1.218.273	1.093.885
University	199.446	182.300	196.904	372.528
Total	8.847.370	12.450.942	8.982.701	8.855.735

Tab. 2: Project Overview for 2023

Leader of the project	Project	Overall project
Dincer	DFG NeuroSENS	303.200
	BMBF MERGE	710.520
Fischer	VW-Stiftung In Situ EC-TEM	952.500
Glunz	BMBF PrEsto	498.030
Helmer	DFG Dynamisch schaltbare Sipropyran Oberflächen	234.200
	DFG Benetzung schaltbarer Oberflächen	247.800
Koltay	DFG 4D-Bioprinting	204.100
Krossing	EU InoChem	1.249.375
Lienkamp	BMBF BioMAMPs	379.680
Milana	Aufblasbare Metamaterialien	164.400
Pappas	DFG Peptid-Systemchemie	193.000
Pelz	DFG MiTEG	321.649
Rapp	EU ERC CaLa	1.999.750
Rühe	DFG Dynamisches Verhalten von Wassertropfen	202.500
	DFG KOMMA	246.250
	DFG PAK (Folgeprojekt)	121.500
	DFG Elastokalorisches Kühlen	272.650
	DFG mTOR2	234.161
Rühe, Rapp at all.	Carl-Zeiss IPROM	4.500.000
Rühe, Speck T., Fischer et al.	DFG livMatS Cluster	6.004.642

Speck, T.	EU ERC GrowBot	348.083
	Carl-Zeiss Deliver	287.034
Vierrath	Vectorstiftung CO2-to-X	1.500.000
	BMBF FC CAT	330.000
	BMBF FC RAT	173.525
Walter	DFG HYBRIDS	159.850
	DFG Synthese , in-operando X-ray	169.550
	DFG IRTG Teilprojekt	16.703

Tab. 3: Budgets of project groups from 2020 until 2023 in €

Project group	2020	2021	2022	2023
Dincer	153.439	286.141	262.021	174.081
Eberl	0	0	0	55.325
Fischer	151.342	116.067	414.418	97.506
Glunz	0	118.617	156.288	171.228
Helmer	30.104	50.680	111.860	160.910
Koltay	138.692	166.018	104.179	10.180
Krossing	50.562	14.821	0	52.404
Lienkamp	285.240	381.203	120.580	23.968
Milana	0	0	0	28.231
Pappas	0	0	24.387	63.875
Pastewka	0	0	48.029	50.424
Pelz	61.853	77.258	86.259	21.251
Rapp	100.530	22.606	355.767	312.750
Rühe	550.142	1.417.754	477.998	500.317
Rühe, Fischer, Speck T. et al.	4.119.000	8.737.000	5.884.000	6.004.642
Speck, T.	98.011	78.254	80.969	123.024
Vierrath	339.089	328.926	358.409	297.613
Walter	66.759	109.159	192.865	63.433
Zapp	0	0	46.997	88.696

HIGHLIGHTS

FUTURE FIELD "ADAPTIVE AND ACTIVE POLYMER MATERIALS"

Towards Snapping Inflatable Metamaterials for Mechanical Intelligence in Soft Machines

Edoardo Milana[1,2], Viacheslav Slesarenko[2]

[1]Laboratory for Soft Machines, Department of Microsystems Engineering, University of Freiburg; [2]Cluster of Excellence *liv*MatS @ FIT – Freiburg Center for Interactive Materials and Bioinspired Technologies

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In the context of Perception and Cognition of robotic sytstems, considerable progresses have been made, yet the domain of Action for robots navigating unstructured environments remains in its infancy. The effectiveness of physical action in such environments is determined through task abilities such as motion agility and endurance. The concept of movement agility is intricately tied to the number of degrees of freedom (DoFs) available to a robotic agent, a realization derived from observing the dynamic motions of living organisms. However, the conventional approach in robotics, wherein centralized control of each DoF through dedicated actuators is employed, encounters challenges as the number of DoFs increases, mainly due to unsustainable energetic costs. This issue is particularly evident in complex legged robots, which, while exhibiting superior agility, incur higher costs of transport (CoT) compared to their wheeled counterparts, compromising their endurance. In stark contrast, living organisms manage to exhibit nimbleness while maintaining energetic efficiency, highlighting a fundamental tradeoff between endurance and agility within our current centralized control architecture.

The inspiration drawn from observing living organisms underscores their heavy reliance on the complex physics of body-environment interaction to execute low-level control tasks, resulting in substantial energy savings [1]. Examples abound, ranging from the passive swing of legs to the recoil of elastic energy stored in tendons, and even the adaptive shape morphing of fish and birds to leverage fluidic drag. These instances highlight the paramount importance of physical characteristics in efficiently executing actions.

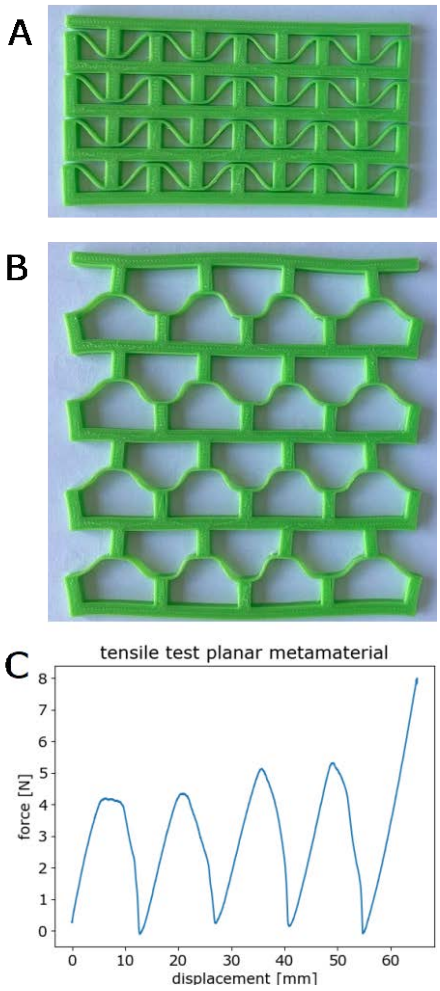

Fig. 1: A. Planar topology flexible mechanical metamaterials at resting state, B. fully snapped stable state. C. Tensile test curve of the metamaterial depicted in subfigures A and B, snap-through instability occurs for each line of unit cells. (© Laboratory for Soft Machines)

This observation has stimulated the emergence of Soft Robotics, a field where a lot of attention is paid to the physical embodiment of robots [2]. Soft Robotics introduces mechanical compliance and underactuation in design, coupled with explorations into new materials, geometries, and control strategies. This effort

entails the development of advanced manufacturing techniques to precisely shape soft materials across multiple scales [3], [4]. Researchers are venturing beyond structural compliance and moving elements, delving into the embedding of control schemes through physical mechanisms [5]. These schemes rely on the complex nonlinear physics of soft materials, encompassing large deformations, reversible snap-through instabilities, and responsiveness to various physical stimuli. Typically, these mechanisms manifest as networks of active or passive soft elements that nonlinearly interact [6], [7], culminating in an overall response corresponding to the desired output, whether it be an oscillation or a preprogrammed sequence.

Within the framework of the DFG Walter Benjamin Program hosted at FIT, the objective of the project “Inflatable Snapping Metamaterials for Next Generation Soft Machines” is to pioneer a new generation of soft machines by designing and manufacturing inflatable snapping actuators that exploit the nonlinear response of architected metamaterials. The tunability inherent in the mechanical metamaterial response allows us to encode novel functionalities into the structure, paving the way for next-generation soft machines with simplified control and embodied intelligence.

This work here presented details our latest achievements within this project, specifically the fabrication and characterization of 3D printed snapping metamaterials. We employ the design and fabrication of flexible metamaterials that undergo snap-through instabilities in tension, thanks to unit cells composed of double-clamped curved beams. The geometry of the unit cell is a key parameter, allowing for the variation of the force required for the snapping motion and, consequently, the programming of response thresholds. Our experimentation involves flexible metamaterials with planar (110 x 60 mm) and cylindrical (55 x φ32 mm) topologies, fabricated using Fused Deposition Modeling (FDM) printing with NinjaFlex materials (TPU 85A). The mechanical response of these metamaterials is thoroughly characterized through uniaxial tests conducted on a Zwick&Roell universal testing machine. Our observations reveal a diverse design space spanning monotonic behavior, monostable snapping, and bistable snapping, underscoring the versatility and potential of this approach. Figure 1 summarizes some experimental results. Subfigure A depicts the flexible metamaterial with planar topology consisting of a 4x4 arrangement of unit-cells.

In subfigure B, the same metamaterial is depicted with all rows in the snapped configurstion, revealing a multistable behaviour. Subfigure C displays the force-displacement characterization of the sample under tension with the testing machine, showing the four force peaks, which identify the snapping instability of each row of the metamaterials. These results represent a first step towards the ultimate goal: to create soft machines with mechanically programmed actuation patterns.

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COLOR3D – Multicolored 3D printing of wood composites by submicron structuring

David Böcherer[1], Yuanyuan Li[1], Sebastian Kluck[1], Niloofar Nekoonam[1], Pang Zhu[1], Dorothea Helmer[1,2,3]

[1]Laboratory of Process Technology, Department for Microsystems Engineering (IMTEK) [2]Freiburg Materials Research Center (FMF) [3]Cluster of Excellence *liv*MatS @ FIT – Freiburg Center for Interactive Materials and Bioinspired Technologies

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As 3D printing becomes more and more popular, it requires a large amount of material and generates considerable amount of waste. So far, most of the commercially available resins for 3D printing are based on fossil resources. Bio-based materials are a promising and more sustainable alternative. As one of the most abundant materials, wood flour has been used as filler for 3D printing of bio-based composite materials. However, wood composite materials are often visually not very appealing and thus they are limited in their applications as everyday products. To equip 3D printed biocomposites with colorful appearance can help to overcome this drawback. As multicolored 3D printing by photoinitiated vat polymerization is still very challenging and requires complicated robitc systems, a modified processing method would be beneficial. Besides the absorption of light by a material, the color of an object can also be controlled by structural coloration, which is used by many animals and plants for their distinctive appearance.

In our work, a new method for the multicolored 3D printing of composite materials by surface structuring was developed.[1] Based on the combination of digital light processing (DLP) 3D printing and nanoimprint technology, macroscopic objects with colorful surfaces by replication of a submicron-structure were fabricated. The novel process technology is based on the layer-by-layer photo curing of a liquid resin with replication of a submicron structure and is shown schematically in Figure 1. To equip the surface of each printed layer with a specific surface structure, a submicron-structured, transparent foil was addd to the bottom of the build tray. When the resin was poured into the build tray, the submicron structure of the foil was filled. By curing of the first layer, the negative structure of the foil was replicated to the surface of the object. After detaching the first layer from the bottom foil, the same procedure of filling the submicron-structured foil with resin, curing the current layer with replication of the structure and detaching was repeated for all the following layers. Thus, every layer was equipped with the submicron structure.

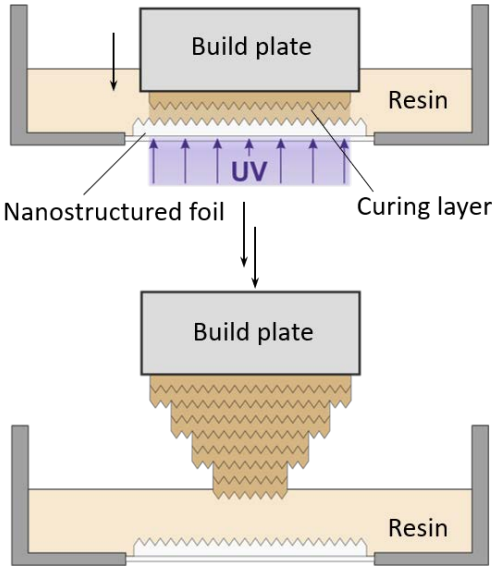

Fig. 1: Schematic illustration of COLOR3D printing process by DLP 3D printing of the individual layers in combination with replication of the submicron-structured foil at the bottom of each layer (© Laboratory of Process Technology).

By selection of a suitable submicron structure for replication to the surface, the 3D printed object can be equipped with a colorful appearance based on structural coloration (Figure 2a). To characterize the replicated structure, the object's surface was analyzed by optical microscopy, scanning electron microscopy (SEM) and white light interferometry (WLI). In the microscopy image in Figure 2b, it can be seen that also on the microscopic level a clear coloration effect is present. By SEM analysis of the surface, a line structure with lattice constant of 1.2 µm was determined (Figure 2c). Besides confirmation of this lattice constant, WLI also showed the height of the replicated

surface structure of 50 nm. In addition to optical and structural properties, the 3D printed objects were also tested for their material properties. The bio-based composites showed a high stiffness of 0.9 - 1.2 GPa. While the addition of up to 5 wt% of wood filler increased the stiffness of the material by 17 %, the addition of 10 wt% of filler decreased its stiffness.

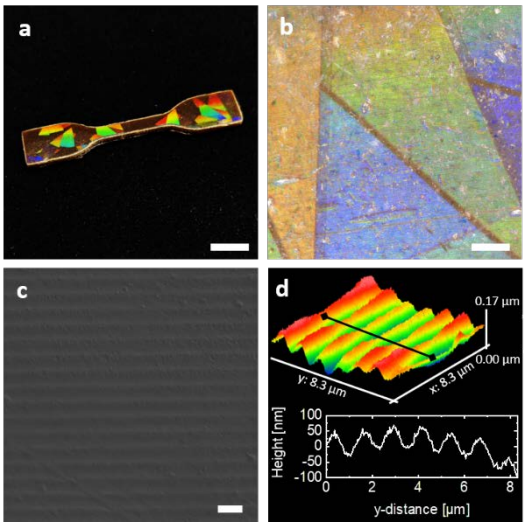

Fig. 2: Analysis of submicron-structured surface of COLOR3D printed wood composite by optical camera (a) optical microscopy (b), SEM (c) and WLI with the corresponding height profile (d) Scale bars: (a) 1 cm, (b) 200 µm, (c) 2 µm. (© Laboratory of Process Technology).

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Development of 3D printable thermoresponsive shape memory artificial Venus flytrap

Falk J. Tauber[1,2], Fabian Scheckenbach[1], Mario Walter[3], Thorsten Pretsch[3], Thomas Speck[1,2]

[1]Plant Biomechanics Group (PBG) @ Botanic Garden of the University of Freiburg; [2]Cluster of Excellence *liv*MatS @ FIT – Freiburg Center for Interactive Materials and Bioinspired Technologies, [3]Synthesis and Polymer Technology Division, Fraunhofer Institute for Applied Polymer Research IAP, Potsdam, Germany

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The Cluster of Excellence "Living, adaptive and energy-autonomous Materials Systems (*liv*MatS)" at the University of Freiburg develops novel materials systems displaying dynamic, life-like and non-equilibrium (energy-autonomous) features. In the *liv*MatS research area of 'Demonstrators,' we aim to create bioinspired prototypes, including an artificial Venus flytrap, to demonstrate the potential of innovative materials systems. We take inspiration from natural materials and their functionalities, using them as 'biological role models' for our bioinspired materials systems. The aim of the research is to apply the functions found in living organisms to engineering applications, allowing for the development of new capabilities such as embodied (physical) intelligence and embodied energy. For example, current artificial Venus flytraps (AVF), which represent soft robotic systems inspired by plants, utilize various plant motion and actuation principles. This includes the use of carnivorous snap trap plants' principles for fast movements [1–5].

In this project, a multilayer thermoresponsive artificial Venus flytrap lobe was developed. Using novel 3D printable shape memory thermoplastic polyurethane (SMTPU) material, developed by the Fraunhofer IAP, in combination with a 3D printable thermoplastic copolyester elastomer (TPC) material with a high thermoexpansion coefficient, we were able to develop the first thermoresponsive multilayer trap lobe that not only closes but also reopens

in response to rise in temperature [6]. The material sheets for the mulitlayer were printed on our *liv*Mats mulitmaterial printing system avalaible at the FIT.

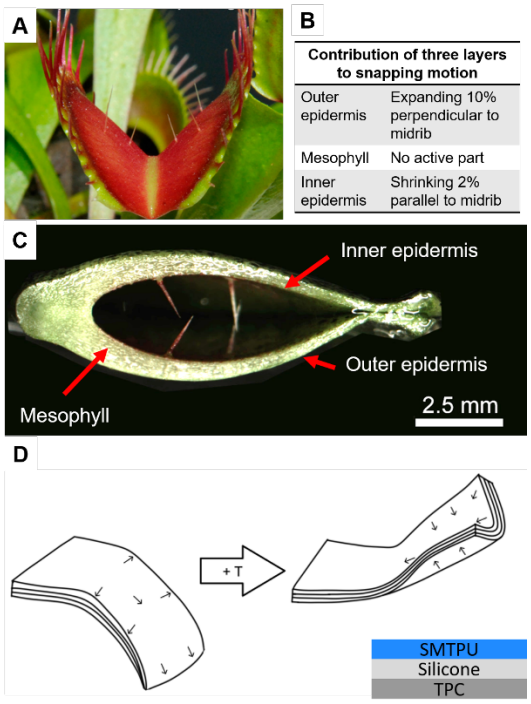

Fig. 1: The *Dionaea muscipula* plant traps are a multilayer material system consisting of three main layers: the outer epidermis (outside), mesophyll (middle), and inner epidermis (inside), which form the trap (A, cross section in C). The prestresses in a trap that is ready to snap are necessary for a fast-snapping motion. The layers contribute differently to the trap closure (B). The multilayer, multimaterial trap lobe demonstrator mimics the three-layer setup and different prestress and expansion ratios of the biological model. It consists of a shape memory thermoplastic polyurethane (SMTPU) and a thermoplastic copolyester elastomer (TPC) connected via non-active silicone layers (D). (Figure reproduced with permission from Springer Nature from [6], Figures A and C are reprinted from publication [7] with permission from PNAS). (© Plant Biomechanics Group)

For the multilayer structure of our AVF traplobe, we took inspiration from the multilayer morphology of the Venus flytrap (*Dionaea muscipula*) snapping traps (Fig. 1 A). The trap consists of three primary tissue layers: the outer epidermis, mesophyll, and inner epidermis (Fig. 1 B). In their study, Sachse et *al*. (2020) investigated the mechanical behavior of these three layers during closure and their respective contributions to trap closure [7]. They observed that closure results from a simultaneous 10% expansion of the outer epidermis and a 2% shrinkage of the inner epidermis. The mesophyll, however, does not actively participate in the closure process but is important as a spacer tissue (Fig. 1 C). The readiness to snap of the trap lobes is achieved through differences in internal hydraulic prestress among the layers of 3:1, which are released during the rapid closing motion [8].

We translated these three layers by using the SMTPU as our contracting “inner epidermis”, a silicone membrane as analogon to the mesophyll representing our spacer layer and the TPC as the expanding “outer epidermis”. Through an extensive characterization of the material properties and a parameter study, we identified the final prestress ratios and thickness ratio required to achieve a change from concave to convex in the artificial Venus flytrap (AVT). To achieve a fast-snapping motion, we integrated these prestress ratios into the multilayer by biaxial prestretching the SMTPU and TPC in a final ratio of 3:1 and a thickness ratio of 3:2 before bonding the layers. The concave trap lobe was successfully achieved (Figure 2A).

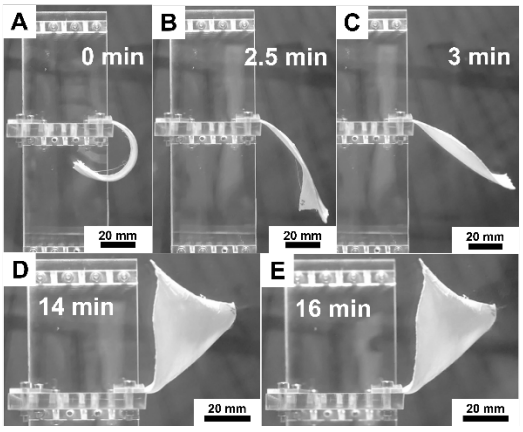

Fig. 2: Exemplary trap lobe motion in response to a rise in temperature to 70°C. At room temperature, the specimen is in the initial concave state (A). Upon increasing the temperature to 70°C, the curvature inversion motion (B) is initiated, resulting in a visible snap (C) and further closure. This achieves a final angular change of 314° (D) after 14 minutes. After maintaining a constant temperature of 70°C for 2 minutes, a relaxation of 10° was observed (E). (Figure reproduced with permission from Springer Nature from [6]) (© Plant Biomechanics Group)

Upon heating above 70°C, the curvature of the lobe changed from concave to convex within 3 minutes (Figure 2B, C), resulting in a final angular change of 314° after 14 minutes (Figure 2D). This change occurred as the 'inner epidermis' (SMTPU) contracted. The traplobe

reopens further upon heating, resulting in a recovery of 40° after 16 minutes. This expansion is due to the outer epidermis (TPC) expanding and the multilayer relaxing (see Figure 2E).

The potential of this thermoresponsive AVT trap lobe lies in the prospect of creating independent AVT systems and supportive frameworks for flexible machines capable of intricate motion sequences. These adaptable autonomous systems could function as supportive structures for soft solar harvesters, safeguarding them against adverse environmental conditions. Furthermore, these grippers could serve as flexible and autonomous devices that respond to dynamic environmental changes by closing and securing the payload.

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Enhancement of photoswitchable wetting properties of porous spiropyran surfaces through roughness engineering

Niloofar Nekoonam[1], Franziska Dreher[2], Dorothea Helmer*[1,2,3]

[1]HelmerLab, Department of Microsystems Engineering; [2]Freiburg Materials Research Center (FMF); [3]Freiburg Center for Interactive Materials and Bioinspired Technologies (FIT)

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Photoswitchable surfaces are of great importance in different applications such as photocontrolled coatings and membranes [1][2]. The photo-induced/photochromic ring opening reaction of Spiropyran (SP) derivatives to Merocyanine (MC) implies a high dipole moment change, making it interesting for photo-controlled wetting properties[3]. However, not only the surface chemistry but also surface roughness determine the wetting properties of a surface and hence, photoswitchable wettability. Here, we demonstrate that the roughness does not necessarily amplify the change in photoswitchable wetting properties[4], and only a certain range of roughness parameters lead to significantly enhanced contact angle changes upon UV light exposure.

We fabricated thin films of porous SP copolymers with five different surface roughness through the polymerization-induced phase separation (PIPS) method[5]. Our synthesized SP monomer was copolymerized with isobutylmethacrylate (IBMA) and ethylene glycol dimethacrylate (EDMA) which served as comonomer and crosslinker, respectively. Varying the crosslinker content from 10 wt% to 30 wt.% in the monomer solution resulted in different pore sizes via PIPS, and hence, various roughness parameters S_a (arithmetic

mean roughness) ranging from 110 nm to 588 nm. Samples are referred to as EDMAX in which X represents the crosslinker content in the monomer solution. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) confirm different pore micro/nano structures and roughness, Fig.1.

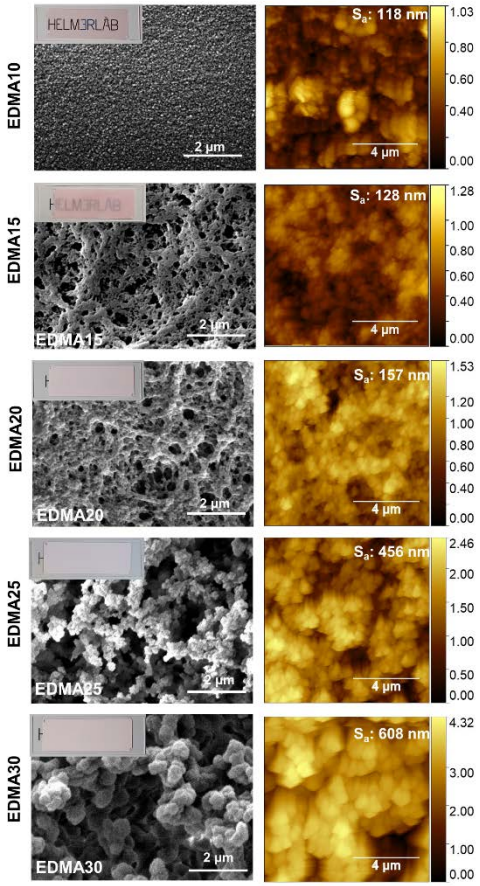

Fig. 1: Surface characterization of SP copolymers with different pore sizes. A) SEM images and B) AFM measurements (lateral scale in µm) of SP copolymers. Increasing EDMA content resulted in larger pore size, i.e. larger roughness parameters (S_a). Insets: Photograph of the SP copolymer thin films. (© HelmerLAB, IMTEK)

Static contact angle (SCA) of a 5 µl water droplet on our SP copolymers revealed a SCA change up to 16 ° before and after UV exposure for EDMA10 and EDMA15 with lower roughness parameters, Fig.2A. Fig.2B presents EDMA10 sample with a circular area switched to MC (more hydrophilic state) on which the droplet showed an obviously lower SCA compared to SP. Interestingly, for EDMA25 and EDMA30 with higher surface roughness an insignificant SCA change was observed. All surfaces were hydrophobic with SCA higher than 110 °. No roll off behavior of droplets on EDMA10 and EDMA15 exhibit Wenzel state, while roll off angles of lower than 30 ° on EDMA25 and EDMA30 indicate Cassie-Baxter wetting state of the droplets.

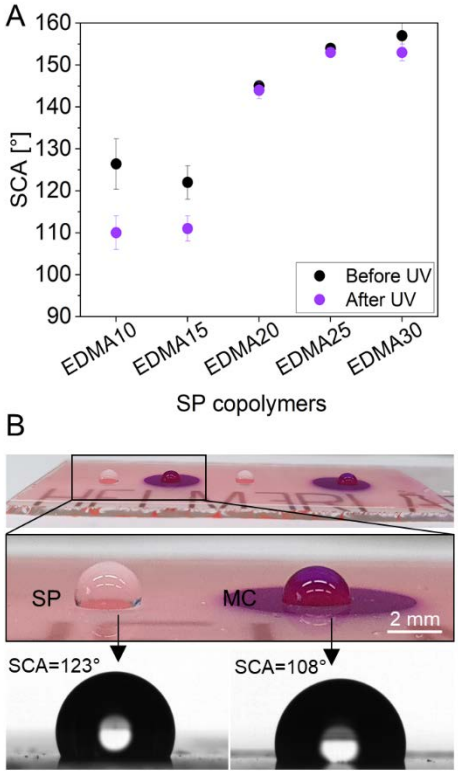

Fig. 2: Photoswitchable wetting properties of our SP copolymers. A) SCA values of SP copolymers with different EDMA content, i.e. different pore size and roughness. B) A circular area on the sample EDMA10 was switched to MC by UV light and the SCA of two 5 µl water droplets was compared. (© HelmerLAB, IMTEK)

As the droplets in the Wenzel wetting state are pinned to the surface and penetrate the nanopores, the droplet wets a larger real surface area with SP/MC groups leading to a more severe influence of change in surface energy upon UV exposure. While in the Cassie-Baxter state droplets are in contact only with asperities and sufficient SP/MC groups are not available to alter the SCA.

We employed our photoswitchable surface EDMA10 to control water vapor condensation patterns on a solid surface. Fig.3 shows switched and unswitched surface 1 min and 10 min after exposure to humidity (at 20 °C and 90% rel.). Droplets merge faster on the switched hydrophilic area, while they preserve the spherical form on the unswitched, more hydrophobic surface.

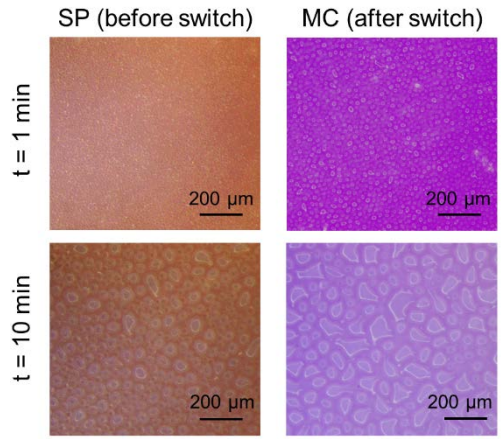

Fig. 3: Water vapor condensation on EDMA10 before and after UV, 1 min and 10 min after exposure to humidity. Larger number od droplets form and coalesce on MC surface. (© HelmerLAB, IMTEK)

In this work, we have shown that only a certain range of roughness parameters lead to high SCA change on photoswitchable surfaces. Further characterization of surfaces revealed that the droplet wetting state (Wenzel or Cassie-Baxter) could influence the effectivity of SP/MC groups as it determined the contact area between the droplet and the surface. Engineering the surface roughness lead to SCA change up to 16 °. Such switchable surfaces have a high potential for use in photo-controlled water vapor condensation.

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Exploiting Self-Contact in Mechanical Metamaterials

David Schwarz[1], Viacheslav Slesarenko[1]

[1]Cluster of Excellence *liv*MatS @ FIT – Freiburg Center for Interactive Materials and Bioinspired Technologies

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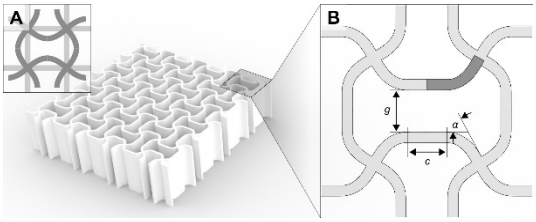

Fig. 1: Metamaterial and design of the unit cell. © created by D. Schwarz, published by Elsevier, unchanged from [5] under CC-BY-4.0 (https://creativecommons.org/licenses/by/4.0/)

Mechanical metamaterials have become a focal point of research due to their ability to exhibit unconventional behaviors when subjected to mechanical loads. One particularly fascinating class of metamaterials is auxetic materials, which possess a negative Poisson's ratio. This unique property distinguishes them from conventional materials, as they contract in all directions when compressed, instead of expanding like typical materials. The intriguing characteristics of auxetic materials have led to their adoption in various industries, ranging from impact protection and sports equipment to biomedical applications and soft robotics [1, 2].

In this study, our primary focus is on a specific type of mechanical metamaterial that features curvy connections [3, 4]. Our objective is to investigate how two critical geometric parameters, namely gap size (representing the space between elements) and contact length (indicating the length of contact between elements), influence the material's mechanical response during compression. These parameters govern the material's behavior, particularly its ability to switch Poisson's ratio during deformation.

Initially, when these materials undergo compression, they exhibit auxetic behavior, contracting in all directions. However, as the compression continues, self-contact between individual elements of the metamaterial takes place at a certain critical strain level. This self-contact results in an abrupt shift of Poisson's ratio, followed by a gradual increase in the width of the specimen. Subsequently, if the compression persists, the material may expand beyond its initial dimensions.

The critical strain at which self-contact occurs is linked to the gap size. Larger gaps require more compression to initiate self-contact, while smaller gaps enable self-contact at lower strain levels. On the other hand, the contact length predominantly influences the magnitude of the jump in the instantaneous Poisson's ratio when self-contact is established. These findings were quantified in finite element simulations and confirmed by mechanical tests of 3D printed specimens.

To underscore the practical implications of our research, we've developed a discrete scales demonstrator. This device harnesses the ability of the metamaterial to switch Poisson's ratio during compression. In this demonstrator, we've utilized four specimens, each with specific geometrical parameters aimed at exhibiting distinct expansion strains. When these specimens are subjected to compression, they illuminate sequentially, providing a clear indication of the level of applied strain. This approach offers a versatile tool for measuring strain or force.

In conclusion, our study [5] offers valuable insights into mechanical metamaterials that can change their Poisson's ratio through self-contact. We've successfully studied the interplay between the unit cell's geometry and resulting mechanical behavior using a combination of finite element simulations and experiments. Furthermore, we've demonstrated the practical applications of our research by developing a scales-like device that utilizes this behavior. Our findings might me implemented in soft robotics or stimuli-responsive materials by enabling precise control and enhanced functionality.

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Inverse design of mechanical metamaterials

Gerrit Felsch[1], Viacheslav Slesarenko[1]

[1]Cluster of Excellence *liv*MatS @ FIT – Freiburg Center for Interactive Materials and Bioinspired Technologies

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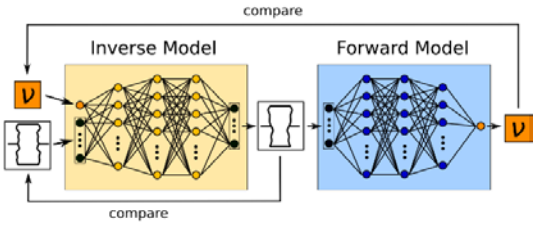

Fig. 1: Framework for inverse design. © created by G. Felsch, CC-BY-4.0 (https://creativecommons.org/licenses/by/4.0/)

Mechanical metamaterials, exemplified by auxetics, display extraordinary behavior due to their intricate internal structures [1]. Auxetics are notable for expanding laterally when stretched, contrary to conventional materials. This unusual behavior is attributed to their internal architecture, which can be based on unit

cells of various designs. These include reentrant, chiral, and other complex structures in both 2D and 3D, that cause auxeticity independently of the base material of the structure.

Traditionally, mechanical metamaterials have been designed using a single unit cell that repeats itself in two or three dimension. Recent advancements, however, allow for more complex structures. For instance, reentrant-hexagonal unit cells exhibit auxetic behavior when configured at specific angles [2]. Changing these angles can switch their properties, offering adaptability but also imposing limitations, as altering unit cell geometry affects the overall size of the metamaterial.

By utilizing unit cells based on curved beams instead of straight ones, it is possible to achieve a broad spectrum of Poisson's ratios while maintaining constant unit cell dimensions. These beams can be represented as Bezier curves, enabling efficient parameterization of the designs [3]. Despite the additional complexity introduced by curved beams for fabrication, advancements in additive manufacturing have simplified their production.

To analytically compute the properties of these structures is challenging, so finite element analysis (FEA) was used instead. The inverse problem—designing a structure for a specific mechanical response—is especially interesting but more challenging. Especially the possibility of multiple designs with the same properties makes this problem complex, as no simple mapping from Poisson's ratio to unit cell exists.

In this project, machine learning was used to address these challenges [4]. A system comprising two neural networks was developed to efficiently predict the mechanical response of the metamaterials with curved beams and to identify geometries that meet specific requirements. The first neural network approximates the relationship between structure and properties. This forward model predicts the Poisson's ratio of a structure, while the second neural network—the inverse model, which is more complex in nature—generates structures that fit the desired properties. While the forward model can be easily trained on structure-property pairs, training the inverse model is more complicated and requires assistance from the forward model.

Training of a neural network requires a dedicated output for each input to the network. This is not the case for the inverse model, where multiple structures can be potential outputs for properties provided as input. The proposed solution for this problem is twofold: the generated structure is fed into the forward model, allowing to establish a unique mapping between the desired and predicted properties. Additionally, the inverse model is supplied with a desired geometry, acting as a selector among the possible solutions.

The effectiveness of these models was evaluated by comparing the predicted mechanical properties with those predicted by FEA. Both the forward and inverse models demonstrated high accuracy both for fitting the properties as well as resembling the desired structure. Therefore, this neural network system not only overcomes the mentioned challenges but also allows expressing a preference for a specific geometry. Moreover, the models enabled the efficient creation of a wide variety of unit cells with identical properties, demonstrating the versatility of the metamaterials based on Bezier curves.

To further validate these models, mechanical tests were conducted on a variety of geometries. The tests compared the desired and actual behavior of 3D-printed specimens. The results confirmed the reliability of the systems in real-world applications.

In conclusion, this project introduced a class of reentrant-hexagonal meta-materials based on curved Bezier beams, alongside a deep learning framework for generating unit cells with specific mechanical properties. The forward and inverse neural network models in this approach are both accurate and computationally efficient, capable of rapidly generating a large number of unit cells. This method for the design and prediction of mechanical metamaterials holds significant potential for various applications.

Integrating curved beams into the unit cell architecture unlocks a broader range of mechanical behaviors while maintaining the

physical dimensions of the metamaterial. This ability to finely tune properties without altering the overall size is particularly advantageous for applications that necessitate varying local mechanical responses while keeping the base material constant.

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Flow Characteristics Improvement in Single Layer Dendritic Microfluidic Networks via Straightforward Modification of Local Elasticity

Efstathios Mitropoulos[1,2], Claas Hendrik-Stamp[1,2], Yutao Zhang[1], Abhishek Srivastava[2], and Thomas Pfohl[1,2]

[1]Department of Physics, University of Freiburg; [2]Cluster of Excellence *liv*MatS @ FIT – Freiburg Center for Interactive Materials and Bioinspired Technologies

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Dendritic structures are widespread in nature, offering a significant advantage in minimizing the pumping power required to facilitate flow from a single point to multiple endpoints [1, 2]. Whether it in river basins or blood vessels, the characteristic of these structures makes them particularly attractive as inspiration for the design of material systems where the transport of substances from an inlet to a number of outlets is required. Such systems do exist in the field of microfluidics where the transport of small volumes of fluids from defined inlets to other parts of a microfluidic chip through microchannels is a core concept of their operation [3]. Polydimethyl-siloxane (PDMS) is a universally accepted well-suited material for use in microfluidic designs [4]. However, PDMS microfluidics face a drawback: a pressure drop per unit length that follows a power law as the diameter decreases. This limitation can be mitigated by incorporating the principles of the constructal law [5] into the design of PDMS microfluidic systems and furtherly enhanced by tuning the local elasticity of the microfluidic channels. By taking the above into consideration, we designed microfluidic dendrites in PDMS that exhibit a number of the associated advantages of similar elastic structures found in nature.

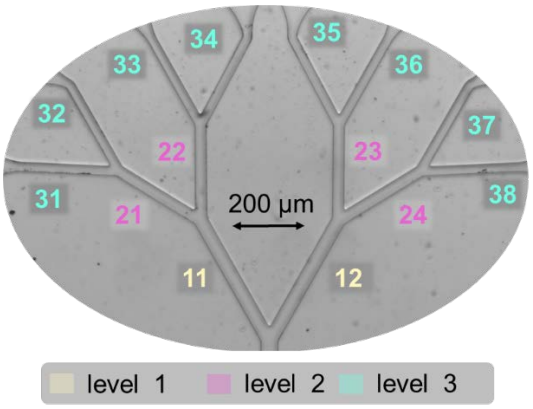

Fig. 1: Design of an optimized network. Widths are chosen based on the constructal law. Numerical indicators are used to identify different branches on the same construct level. © Pfohl Group

The core design of our microfluidics dendrites is presented in Figure 1. A microfluidic channel undergoes bifurcation thrice. The width of each channel is following the relation $D_{i+1}/D_i = 1/\sqrt[3]{2}$, where D_i is the diameter of the channel of a given level and D_{i+1} the diameter referring to the subsequent level [6]. The bifurcation angle (59º) as well as the volume of the channel network and the length of the channels were chosen as design parameters, the height of the devices was 200 µm. The devices were fabricated via replica molding.

Controlling PDMS’ elastic modulus through the precursor/curing agent weight ratio is well

established, but leads to complications when the tuning of local elasticity is desired. Here, we overcame this problem in a simple yet effective and easy to implement manner. Solid channel walls were replaced by 20 µm thick membranes by implementing hollow chambers (Figure 2) only in desired areas around the channels. Thus, the membranes deflect, in response to pressure applied to the membranes, increasing the channel width and resulting in an overall increase of the hydrodynamic conductivity.

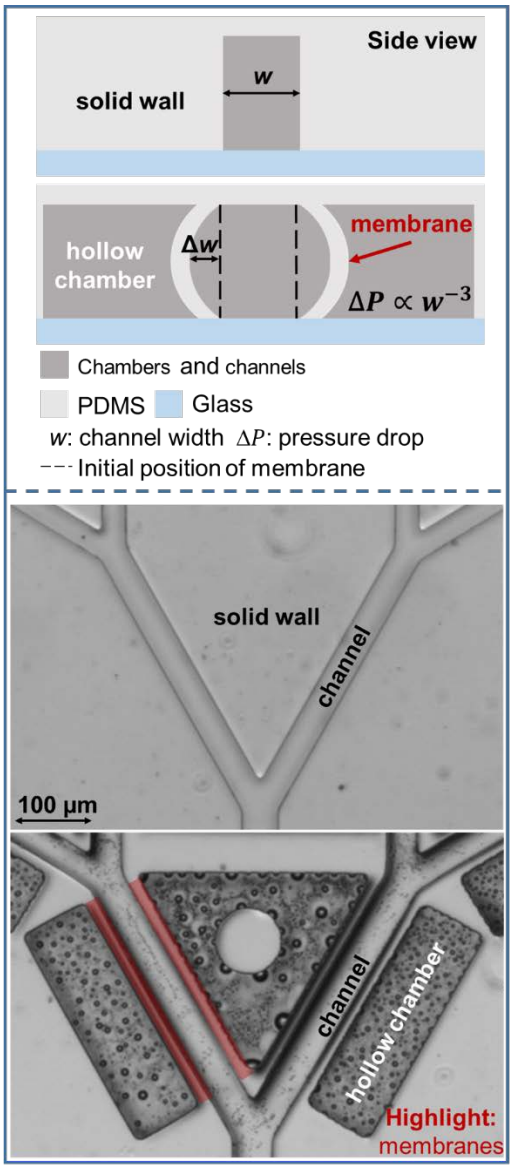

Fig. 2: Working principle of tuning local elasticity in a single layer (top). Resulting structures after replica molding (bottom) with water flowing through the channels. © Pfohl Group

To study the improvement in flow rate for our designs, a device with solid walls and a device, in which all dendritic levels had membranes (holoelastic), were studied under three different pressure-driven flow profiles. A sinusoidal profile with a period of 2 s, a symmetric square pulse train profile with a period of 2 s and a steady state pressure profile. Each experiment was repeated for different maximum values for each profile. Water was chosen as the working fluid because it is biocompatible and most systems in nature transport some aqueous solution. Image analysis in ImageJ and Matlab was used to calculate the hydrodynamic conductivity for each dendritic level and the total hydrodynamic resistance and conductivity of each device were calculated after measuring the width of different dendritic branches.

Plots of the calculated hydrodynamic resistance on branch 11 for three different pressure maxima under the sinusoidal and square pulse signals are shown in Figure 3. In both cases, a decrease in resistance associated with the deflection of membranes is observed with increasing pressure. The total hydrodynamic conductivity versus the maximum supplied pressure for a solid wall device and a holoelastic device under the three different pressure profiles is shown in Figure 4. For the latter device, a substantial increase of up to 45 % can be observed for the hydrodynamic conductivity of the steady state pressure profile.

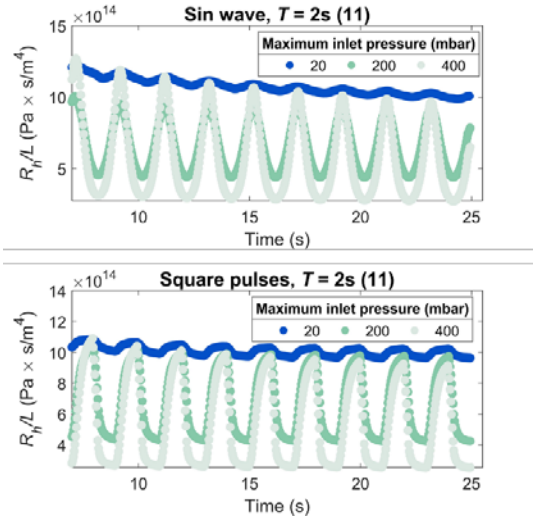

Fig. 3: Temporal evolution of hydrodynamic resistance in branch 11 of a holoelastic device under a sinusoidal (top) and square pulse train (bottom). Minimum values are achieved for the highest applied pressure. © Pfohl Group

The results above prove that the holoelastic devices exhibit substantially improved flow characteristics compared to their more traditional solid wall counterparts. Thus, they are able to provide higher flow rates for similar flow conditions. The aforementioned improvement in flow characteristics is strongly non-linear and as such could play the role of a cornerstone mechanism to not only increase, but also direct and redirect flow in microfluidic devices under different applied pressures. In addition, the ability to impose periodic flow profiles on the movement of the membranes opens up the possibility of closely mimicking the flow behavior of elastic living systems such as blood vessels in material systems.

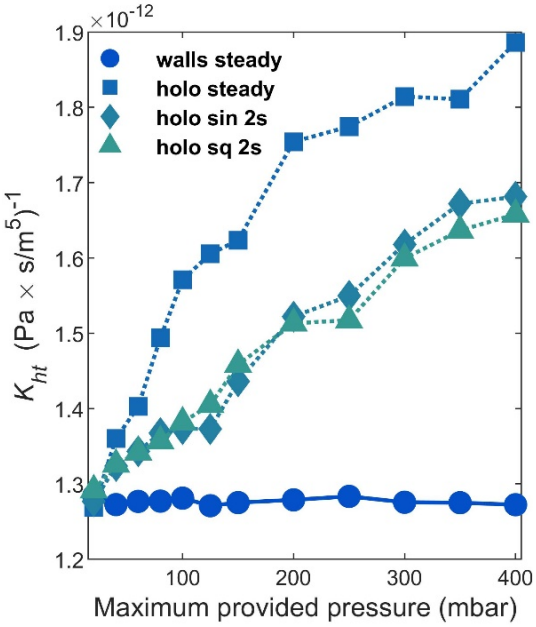

Fig. 4: Total hydrodynamic conductivity versus pressure calculated under a steady applied pressure profile for the solid walls device and for sinusoidal, square pulse train and steady applied pressure profiles for the holoelastic device. A maximum improvement of up to 45 % can be observed for the hydrodynamic conductivity. © Pfohl Group

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Fluidity in Form: Exploring Elastic Membrane Dynamics under Solvent Symphony

Abhishek Srivastava[1], Claas Hendrik-Stamp[1], Efstathios Mitropoulos[1,2] and Thomas Pfohl[1,2]

[1]Cluster of Excellence *liv*MatS @ FIT – Freiburg Center for Interactive Materials and Bioinspired Technologies; [2]Department of Physics, University of Freiburg

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Microfluidics, a multidisciplinary field at the intersection of physics, chemistry, engineering, and biology, has emerged as a powerful tool for manipulating and studying minute volumes of fluids. This technology enables precise control of fluidic environments on the micron scale, with applications ranging from medical diagnostics to chemical synthesis. At the forefront of this technological evolution is the exploration of elastic membranes in microfluidics.

These elastic elements, characterized by their flexibility and adaptability, hold great promise for a myriad of applications. Among these applications, the utilization of elastic membranes is emerging prominently in the development of microfluidic sensors [1]. These membranes serve as fundamental components in intricate microfluidic networks [2-4]. Additionally, their adaptable nature plays a crucial role in surface charge sensitive nano-trapping and sorting methods [5,6]. Elastic membranes offer opportunities for innovations in healthcare diagnostics, drug delivery, lab-on-a-chip technologies, and environmental monitoring.

As we delve into the details of our experimental setup and results, this report aims to contribute valuable insights into the interplay between PDMS (polydimethyl-siloxane) membranes and isopropanol/water mixtures, shed light on the potential implications for microfluidic systems, and provide a foundation for further exploration in this dynamic field.

In our specific microfluidic design (Fig. 1), two upright standing membranes are incorporated into the device. These membranes are meticulously fabricated to be bonded at their ends, ensuring structural integrity and stability. Each membrane is precisely set to a standardized length of 1 cm and a height *b* of 100 µm, ensuring consistent and controlled experimental conditions within the microfluidic device.

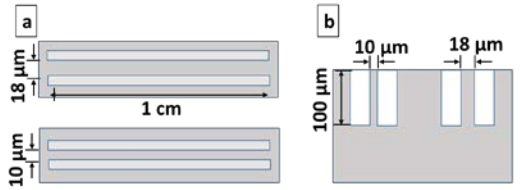

Fig. 1: Illustration depicting the configuration of the PDMS microfluidic device. (a) Top view displaying two vertically oriented membranes of 10 µm and 18 µm thickness *h*, each 1 cm long. (b) Side view with the membrane height *b* set to 100 µm. © Pfohl Group

Furthermore, to simulate the different conditions relevant to our experimental objectives, the membranes exhibit distinct thicknesses *h*, 10 µm and 18 µm. This deliberate variation in thickness allows us to explore the effect of membrane dimensions on buckling behavior in response to changing solvent conditions.

In the experiment, a microfluidic device containing adjacent elastic membranes (10 µm and 18 µm thick) is positioned under a microscope for controlled observations. A small, precisely measured volume of an isopropanol/ water mixture, the chosen solvent, is then applied to the top surface of the elastic membranes within the microfluidic device (Fig. 2). Immediately after the solvent introduction, a glass coverslip is placed over the solvent-exposed area of the microfluidic device, creating a sealed environment.

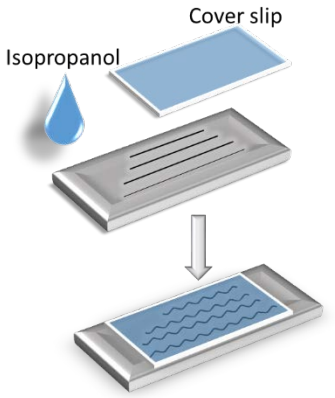

Fig. 2: Schematic representation of the step-by-step experimental procedure, illustrating the systematic process from the placement of the microfluidic device to the observation of the membrane response under varying isopropanol/ water volume fractions. © Pfohl Group

The response of the membranes to the solvent in the microfluidic setup is imaged by microscopy. Significantly, the investigation reveals interesting observations regarding the buckling behavior of the membranes. The isopropanol volume fraction (ϕ_{iso}) of the solvent mixture is systematically varied from 0.952 to 1.0, leading to distinctive results (Fig. 3).

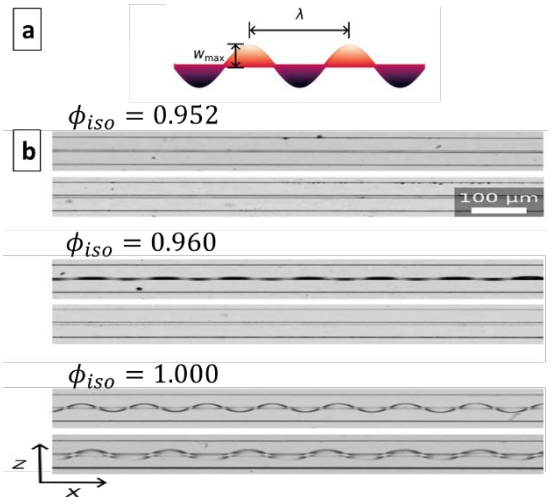

Fig. 3: (a) Schematic representation of the membrane buckling dynamics with amplitude as w_{max} and wavelength as λ, (b) microscopic images capturing the dynamic response of the membrane at different volume fractions of isopropanol, revealing distinct morphological changes in the buckling behavior. © Pfohl Group

Initially, for ϕ_{iso} = 0.952, no buckling is observed in either the 10 µm or 18 µm membranes within the microfluidic device. However, as ϕ_i increases to 0.960, a slight buckling is observed in the 10 µm membrane, while

the 18 µm membrane remains unaffected within the same microfluidic device. For ϕ_{iso} = 1.0, buckling is observed in both membranes on the microfluidic device. Importantly, at ϕ_{iso} = 0.96, buckling initiates in both membranes within the microfluidic device. Interestingly, the wavelengths of membrane buckling remain constant with increasing volume fraction for both membranes on the same microfluidic device, as shown in Fig. 4(a).

Further analysis shows that for lower volume concentrations below ϕ_{iso} = 0.96, the buckling amplitude is zero. However, beyond this concentration, the amplitude steadily increases for both the 10 µm and 18 µm membranes in the microfluidic device and converges at ϕ_{iso} = 1, as shown in Fig. 4(b).

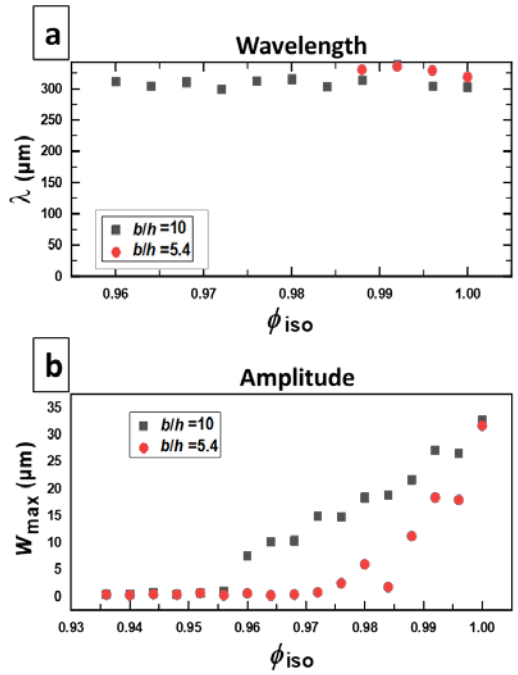

Fig. 4: Graphical representation of (a) wavelength variations and (b) amplitude variations with changes in the volume fraction of isopropanol. © Pfohl Group

When a straight membrane is exposed to an isopropanol-water mixture, it swells. Based on the swelling factor γ > 1, the volume of the membrane increases, and the lateral stress σ inside the membrane can be described in terms of Young's modulus *E* and the Poisson's ratio ν as [8]

$$\sigma = \frac{E(\gamma-1)}{1-\nu} \quad (1).$$

Use of the theory of elastic stability for thin plates [2,9],

$$\sigma_b = \frac{kE}{12(1-\nu^2)}\left(\frac{h}{b}\right)^2 \quad (2),$$

where σ_b is the stress at the buckling point and *k* is the dimensionless buckling coefficient.

Comparing σ and σ_b reveals that the critical value of γ leading to membrane buckling depends on the inverse of the aspect ratio, given by [2]

$$(\gamma - 1) \propto \left(\frac{b}{h}\right)^{-2} \quad (3).$$

This relationship offers a pathway for deliberately induce buckling in specific spatial segments or membranes within microfluidic devices at a defined solvent composition by manipulating the aspect ratio.

This study not only contributes to the fundamental understanding of membrane behavior in microfluidic systems, but also highlights the potential applications of such insights in the design of advanced microfluidic sensors and actuators, e.g., solvent-specific (tuned by the volume fraction and *b*/h) mechanical sensor, which can be modified to an optical sensor using deflection/scattering of light due to the buckling.

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3D printing of high-resolution microfluidics at the centimeter-scale

Christof Rein[1], Frederik Kotz-Helmer[*1,2], Bastian E. Rapp[1,2,3]

[1]Laboratory of Process Technology (Neptun Lab), Department of Microsystems Engineering; [2]Freiburg Materials Research Center (FMF); [3]Freiburg Center for Interactive Materials and Bioinspired Technologies (FIT)

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The advent of stereolithography (SL) for 3D printing microfluidic chips has gained much attention during the last decade, as SL has the potential to replace traditional fabrication methods like soft lithography [1]. Microchip manufacturing using SL does not require an additional bonding step like a fabrication in PDMS calls for, additionally unlike soft lithography, SL allows manufacturing oftruly arbitrary designs [2]. Due to a fast cycle between 3D model generation and rapid one-step fabrication, SL is believed to drastically shorten the *concept-to-chip* time for the development of new microfluidic prototypes [3].

One major obstacle is the inaccessibility of both high resolution below 100 µm in order to access the truly microfluidic regime and also printing on a large lateral size, required for most microfluidics, at the same time[4].

Within this work we demonstrate for the first time that utilizing a laser-based SL it is possible to fabricate high-resolution microfluidics with a channel width below 100 µm, but also with a channel length of up to 7 cm. The device is equipped with a 405 nm laser mounted on a XY-stage that can translate on a 10 x 10 cm² plane and switch between a high-resolution 5 µm beam and a lower resolution 40 µm beam. In order to achieve a high resolution, a low-viscosity photoresist based on the monomer poly(ethylene glycol) diacrylate (M_w = 250) was calibrated for a high in-plane resolution and out-of-plane resolution by adjusting the writing parameters and UV-absorber content. Multiple calibration structures were printed and a wide range of dose parameters were screened in order to choose the setting for laser power and velocity with the highest accordance to CAD values (Fig. 1).

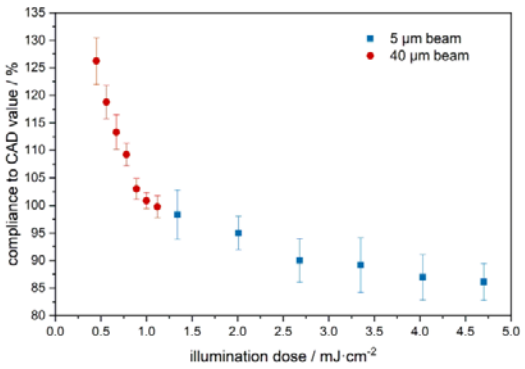

Fig. 1: Accordance of 3D printed calibration structure dimensions to the CAD dimensions. Both the high-resolution 5 µm beam and the lower resolution 40 µm beam show the closest accordance around 1.2 mJ·cm^{-2}. (© Neptunlab, IMTEK)

In order to reduce the Z-overcuring error a strategy was developed that fabricated the roof layers of embedded channels with a lower dose, which was sequentially increased during fabrication. By optimizing the dose parameters and dose increase steps the Z-overcure was reduced to around 1 µm, thus resulting in embedded channels with a height closely matching the CAD-dimensions. Microchannels with a width of 21 µm and a height of 30 µm were fabricated and functionality displayed by filling them with dyed water (Fig. 2A,B).

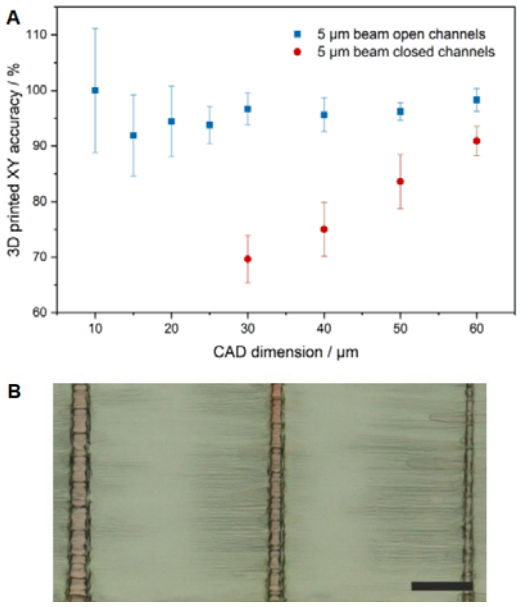

Fig. 2: 3D printed microchannels and achieved XY accuracy of the high-resolution 5 µm beam. (A) Channel width of open and embedded channels compared to the corresponding CAD dimensions. Embedded channels can be printed down to a CAD dimension of 30 µm, resulting in a 3D printed channel width of 21 µm. (B) 3D printed microchannels down to 21 µm filled with red dye. Scale bar 100 µm. (© Neptunlab, IMTEK)

Additional strategies were developed that enabled the fabrication of channel geometries with aspect ratios of 0.1 (Fig. 3A) or 10 (Fig. 3B). Utilizing conventional printing strategies the reduced dose required for writing the roof layers would also have reduced the overall layer-to-layer adhesion and mechanical strength of the bulk phase. Additionally, writing a high-resolution vertical microchannel requires the utilization of the 5 µm beam for every layer, which increases fabrication time. Therefore, the writing with spatially controlled parameters like high-resolution or reduced dose was decoupled from printing the bulk phase by manipulation of the CAD file. The region that required a tailed 3D printing strategy was cut out from the STL file and utilized as a second STL file, whose parameters could be addressed individually. This way, both high-aspect ratio channels were printed with high accuracy to the CAD values.

In order to demonstrate the fabrication of microfluidic chips that both combine a centimeter, scale lateral footprint as well as sub-100 µm microchannels a 7 cm length microfluidic mixer was printed. The dose was increased to artificially decrease the channel width down from 100 µm to 77 µm (Fig. 4A). Functionality was demonstrated by perfusing the microfluidic mixer with a yellow and blue dye at a flowrate of 0.1 µl per minute (Fig. 4B).

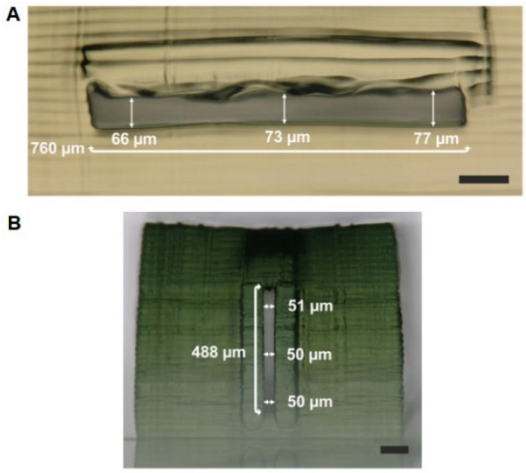

Fig. 3: Different aspect ratio microchannels fabricated with a custom 3D printing strategy. (A) Microchannel with an aspect ratio of 0.1, printed by in-plane manipulation of the illumination dose. (B) Microchannel with an aspect ratio of 10, printed by in-plane manipulation of the beam size. Scale bars 100 µm. (© Neptunlab, IMTEK)

In this work, we have successfully utilized a commercial SLA in order to fabricate microchips that for the first time combine high resolution microchannels and a previously unmatched XY chip dimension. Additional strategies were developed that allowed in-plane manipulation of the illumination dose and 3D printed resolution. This work will facilitate fabrication of lab-scale of microfluidic chips.

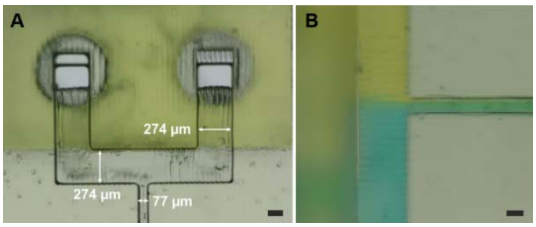

Fig. 4: 3D printed microfluidic mixer. (A) Microchip inlet displaying the reduced channel width of 77 µm. (B) Microchip perfused with yellow and blue dye at a flowrate of 0.1 µ/min. Both liquids mix readily due to the small volume. Scale bars 100 µm. (© Neptunlab, IMTEK)

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Microstructure fabrication on hydrogel surface via dehydration of double network hydrogels

Pang Zhu[1], Dorothea Helmer[1,2;3], Bastian E. Rapp[1,2,3]

[1] Laboratory of Process Technology, NeptunLab, Department of Microsystems Engineering (IMTEK); [2] Freiburg Center of Interactive Materials and Bioinspired Technologies（FIT; [3] Freiburg Materials Research Center (FMF).

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Creatures change surface microstructures dynamicly in response to stimuli [1][2]. This self-growth mechanism is used for designing biomimetic materials with specific surface microstructures and promising applications. For example, Gong *et al*. utilized force triggered free radical polymerization to grow microstructures on double network hdyrogels. Profiles of microstructures can be controlled by adjusting conditions of applied stimuli, like size and shape of microindenters and indention depth[3]. Compared with force, light is a more controllable stimulus, which can be applied to materials remotely and achieves precise spatial and temporal control thanks to masks and switches[4]. Albertus *et al*. fabricated a photoresponsive hydrogel which contains photochromic spiropyran. Upon being illuminated by visible light, hydrogels change their surface topography owing to the hydrophilicity change caused by light-induced isomerization of spiropyran[5]. However, these fabricated microstruces exhibit rough and irregular profiles. Facile methods to obtain microstructures with more controllable size and high surface quality on hydrogels are still highly sought-after.

Here, we introduce a straightforward method for fabricating microstructures via dehydration of double network hydrogels. This approach demands minimal equipment and relies on readily available common acrylic chemicals and initiators. As illustrated in Fig.1. The first network hydrogel (1st NH) (Fig.1a) which primarily consists of sodium acrylate was immersed into the pre-gel solution of the second network hydrogel (2nd NH) (Fig.1b) which consists of 2-hydroxyethyl methacrylate (HEMA) to reach the swelling equilibrium state. To define the microstructure patterns, the hydrogel was illuminated by UV light, the obtained double network hydrogel (DNH) was then immersed into water for 24 h in order to remove unpolymerized chemicals. The DNH was immersed into hydrochloric acid (HCl) solution to induce gel shrinkage and achieve the final microstructure.

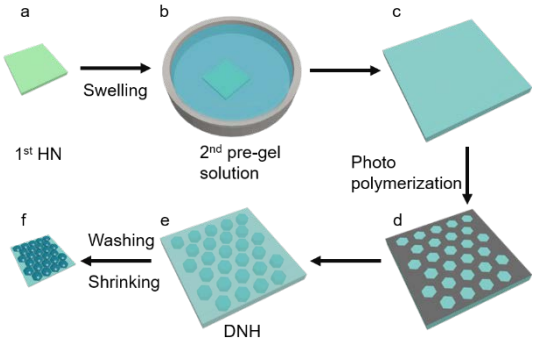

Fig. 1: Schematic illustration of fabricating microstructured surface via dehydration of double network hydrogel. The first hydrogel network (1st HN, (a)) is immersed into 2nd pre-gel solution (b) to reach a fully swollen state (c); photo polymerization of the second hydrogel network (2nd HN) is conducted via UV illumination under a physical mask to get a double network hydrogel (DNH) (d); after immersing the DNH (e) into HCl solution, the microstructured surface (f) is obtained owing to different shrinkage ratios between the illuminated areas and unilluminated areas. (© Neptunlab, IMTEK)

As shown in Fig. 2a, after photo polymerization using a physical mask with a micro-hexagon array, the transparent 1st NH transformed into a whitish appearance due to the formation of the 2nd NH composed of HEMA. Upon exposure to the HCl solution, the size of DNH decreased significantly. The surface topography of the shrunken hydrogel was characterized using the white light interferometer (WLI) (Fig. 2b). The fabricated micro-hexagon structures exhibited uniformity and smoothness with a diameter of 56.5 µm and structural

depth of 11.2 µm. The profiles of microstructures can be controlled by adjusting illumination time. Extended illumination times led to an increase in both the diameter of the micro-hexagon structure (from 56.5 µm to 105 µm) and the height (from 11.2 µm to 18.2 µm).

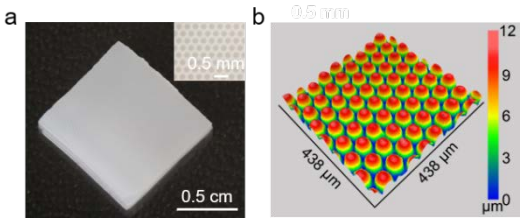

Fig. 2: Microstructured surface characterization. (a) The optical picture of DNH and the microscope image (inset); (b) 3D structure of the microstructure obtained via WLI. (© Neptunlab, IMTEK)

Our materials can be employed as a mold for fabricating a PDMS microlens array (MLA) using soft lithography. Fig. 3 shows each microlens of the PDMS MLA can project a sharp image, which not only demonstrates the high surface quality and uniformity of the PDMS MLA, but also the potential application of the microstructure fabrication method in optical engineering field.

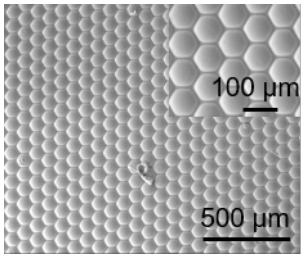

Fig. 3: Optical application illustration of the microfabrication method. SEM images of the replicated PDMS microlens array under different magnifications. (© Neptunlab, IMTEK)

In summary, we introduce a straightforward method for the fabrication of patterned hydrogels through the dehydration of double network hydrogels, which eliminates the need for complex equipment and intricate chemical synthesis. The morphology and profile of fabricated microstructures can be easily controlled by varying illumination time and masks employed during photopolymerization. We also successfully fabricated a PDMS MLA using the structured hydrogel as a mould through soft lithography technology, which shows exceptional surface quality and imaging performance.

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-Push, Push, Push- Cooperative Actuators and Actuators Fields by Direct Writing Processes

Nicolas Geid, Jürgen Rühe

Chemistry and Physics of Interfaces, Department of Microsystems Engineering, University of Freiburg, Georges Koehler Allee 103, 79110 Freiburg, Germany

Project funding: Deutsche Forschungsgemeinschaft (DFG)

The generation of microactuators is of great interest, especially in the fields of soft robotics[1] and lab-on-chip applications[2].

In a previous work, our group already fabricated magnetic microactuators to produce fluid transport without external pumps. These so called artificial cilia were produced with a mask based photolithographic process out of prepolymeres.[3,4] A reactive group in the prepolymer can be activated by UV light and a C,H-insertion reaction leads to crosslinking into neighboring chains as well as covalent attachment to the surface (Figure 1a). This entire process takes place in the glass-like state of a polymer coating.[5]

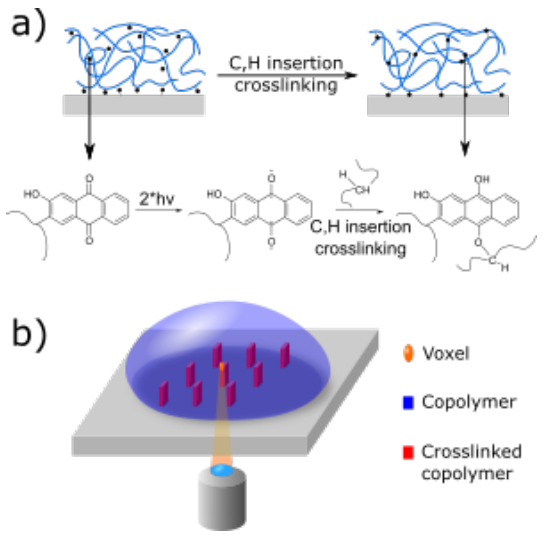

Fig. 1: Schematic representation of a) the C,H-insertion reaction of a reactive group (anthraquinone derivate) via a biradical transition state and b) the direct writing into a polymer layer by Two photon crosslinking (2PC). © CPI, IMTEK Univ. of Freiburg.

With a direct writing process, the flexibility for designing microactuators in any desired shape could be heavily increased. Two photon crosslinking (2PC) based on two photon lithography and the C,H-insertion crosslinking (Chic) is a powerful tool for direct writing of polymeric structures (Figure 1b). In another work, our group already showed, that 2PC of prepolymers based on anthraquinones leads to well defined microstructures.[6]

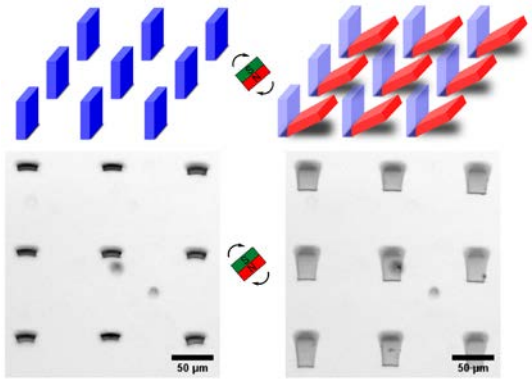

Fig. 2: Schematic illustration and light microscopy images of beam-like magnetic microactuators written with 2PC and actuated under a rotating external magnetic field. © CPI, IMTEK Univ. of Freiburg.

Using the same prepolymers combined with superparamagnetic nanoparticles, it is possible to print microactuators out of a polymer-nanoparticle composite in one step. These microactuators can then be moved by a rotating external magnetic field (Figure 2). Parameters for printing (to example energy dose) and for the composite composition (nanoparticle content, crosslinker content in the polymer, molecular weight) are important in consideration of the resulting stability and mobility of the microactuators in a magnetic field.

A major goal is to investigate the movement of microactuators in relation to different geometries. These can be easily adapted using this method, as shown in Figure 3. By varying the width from left to right (1-6 µm), the actuation can be strongly influenced.[7] However, more complex structures can also be easily produced with this method and correlations between particle volume, area moment of inertia and geometry of the structures to the actuation will be studied.

Furthermore, multi-material actuators are also to be written which, for example, have an anchor with better water solubility or can also react to several stimuli.

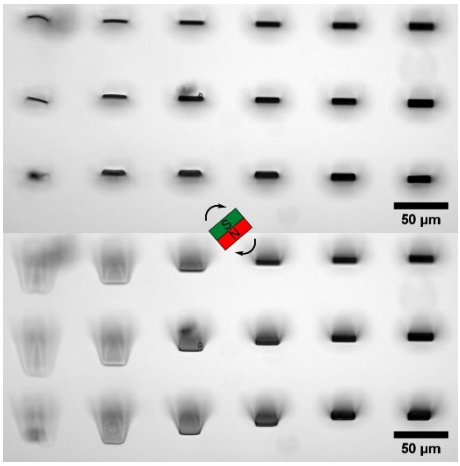

Fig. 3: Light microscopy images of beam-like microactuators of different thicknesses from left to right (1-6 µm), which are moving in a rotating external magnetic field. © CPI, IMTEK Univ. of Freiburg.

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Hot stamping of polymer coatings to produce surface attached and 3D-structured polymer networks using CHic Chemistry

Alexander Bleiziffer[1,2,3] and Jürgen Rühe[1,2,3*]

[1]Department of Microsystems Engineering (IMTEK), Laboratory for Chemistry & Physics of Interfaces; [2]Freiburg Institute for Interactive Materials and Bioinspired Technologies (FIT); [2]Cluster of Excellence *liv*MatS @ FIT – Freiburg Center for Interactive Materials and Bioinspired Technologies

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Photolithography is an important process in semiconductor technology to create structured surfaces, but often requires specific substrate materials that have to be pre-treated. Using a novel, fast and simple process based on the crosslinking of thermally reactive pre-polymers, we were able to produce spatially controlled surface-bound polymer networks on a variety of different common materials.[1]

In this process, which is similar to branding livestock or wood with a hot branding iron, a hot stamp is brought into direct contact with a diazo group-containing copolymer film deposited on a substrate to map the profile of the stamp into the polymer film. Crosslinking and covalent surface attachment to the substrate are achieved as a result of thermal activation of the diazo groups, leading to carbene formation, which induces C,H-insertion crosslinking (CHic) within the layer and across the interface to the polymeric substrate.[1–3]

A washing step removes all the uncrosslinked material, leaving behind the shape of the stamp which is transferred into the polymer film. The polymer systems used here allow activation of the diazo function at mild temperatures, so that relatively fast processing allows step-and-repeat processes.

The advantage of this system is that crosslinking takes place in the glassy state. Therefore, there is no shrinkage as as often observed in nanoimprint lithography. In addition, unlike photolithography, opaque or thick layers can also be structured.[4,5]

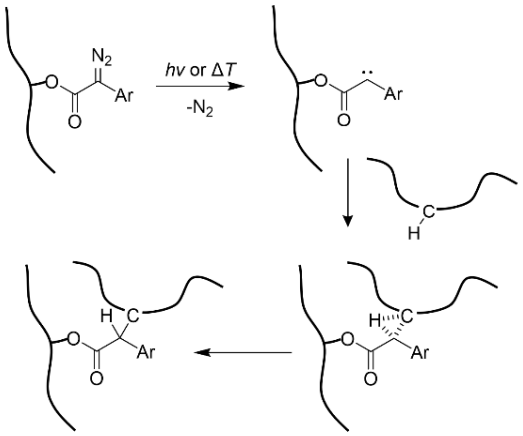

Fig. 4: Schematic representation of the C,H-insertion reaction upon thermal activation of the diazo group © CPI, IMTEK Univ. of Freiburg.

The diazophenyl ester crosslinker PEDAZ and its derivatives can be copolymerized with common methacrylate monomers, and the resulting copolymers can be activated and crosslinked at rather low temperatures.[6] The activation energy for diazo decomposition can be further reduced by substituting the aromatic part e.g. with a methoxy group in para position, so that thermal structuring takes place within a few seconds and heat propagation is spatially contained, resulting in high-resolution structures. This is illustrated in Figure 2 in the form of ring structures produced by contact with a heated aluminum hollow cylinder.

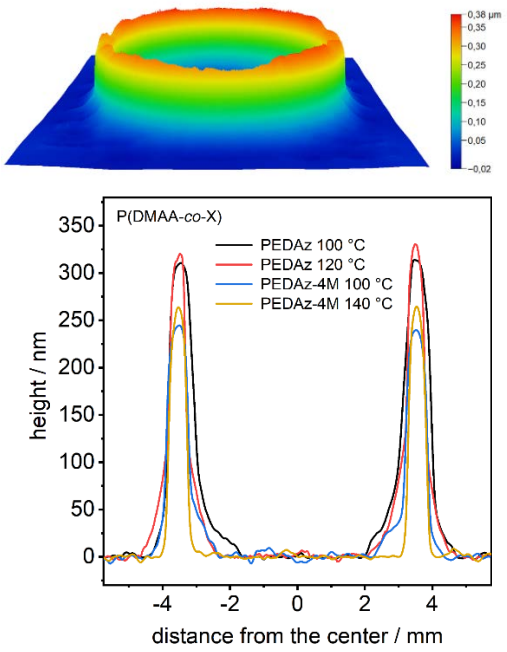

Fig. 5: Top: White light interferometer images (WLI) of thermally structured P(DMAA-co-PEDAz). Bottom: Height profiles of the rings obtained by thermal structuring at constant conversion. Increasing the temperature and use of the more reactive crosslinker PEDAz-4M improves the resolution. © CPI, IMTEK Univ. of Freiburg.

In addition to simple ring structures, more challenging structures can also be depicted using this method, such as pillars in the micrometer range. Dynamic structuring is also possible using a similar roll-to-roll process. By constantly moving a microstructured roll over a coated substrate, the pattern of the roll could be imaged with good resolution, as shown in Figure 3.

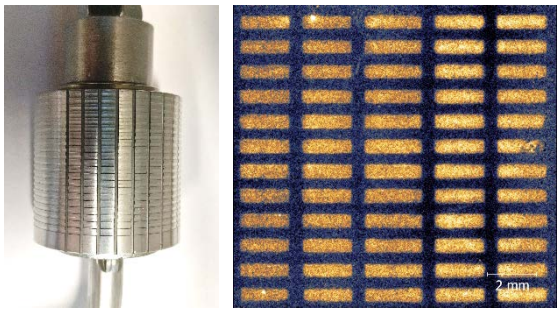

Fig. 6: Structured aluminum roll and a fluorescence microscopy image of a substrate patterned by a roll-to-roll process. © CPI, IMTEK Univ. of Freiburg.

Another aim of this research is structuring using thermal scanning probe lithography (t-SPL) to create nanometer-sized features. The CHic-able polymers can act as negative photoresists, which does not yet exist in the field of t-SPL.

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Thermal crosslinking of paper fibers to generate wet strengthened and multifunctional paper

Florian Pakusch[1], Jürgen Rühe[1,2], Markus Biesalski[3]

[1]Laboratory for Chemistry & Physics of Interfaces, Department of Microsystems Engineering (IMTEK), University of Freiburg, 79110 Freiburg, Germany; [2]Cluster of Excellence *liv*MatS @ FIT – Freiburg Center for Interactive Materials and Bioinspired Technologies; [3]Makromolecular and paper chemistry, TU Darmstadt, Alarich-Weiss-Straße 8, 64287 Darmstadt, Germany

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Paper loses ~90 % of its mechanical strength when completely soaked with water.[1] Therefore, it is important to modify paper with wet strengthening agents in a wide variety of applications such as paper towels, bank notes, map paper, tissue paper or packaging paper.[2,3] Even though, wet strength agents are already widely used the exact mechanism of

wet strengthening of paper is not fully understood.

In the literature two mechanism are proposed for the wet strength of paper.[4]

- The protection mechanism: polymer forms a layer around the paper fibers which inhibits the ability to swell
- The reinforcement mechanism: polymer is mainly at fiber-fiber cross sections and forms cuffs which increase fiber-fiber interaction

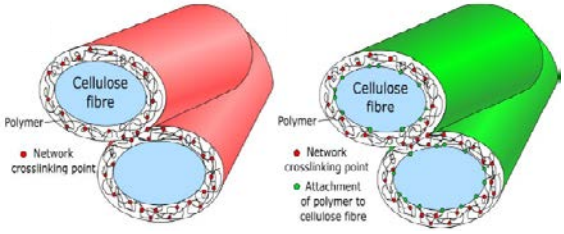

Fig. 1: Schematic depiction of wet strength mechanism: protection mechanism (left side in red) and reinforcement mechanism (right side in green) © CPI, IMTEK Univ. of Freiburg

In a previous work from our group the distribution of the wet strength agent inside the paper was investigated using confocal laser scanning microscopy (CLSM) and rhodamine B labeled polymer.

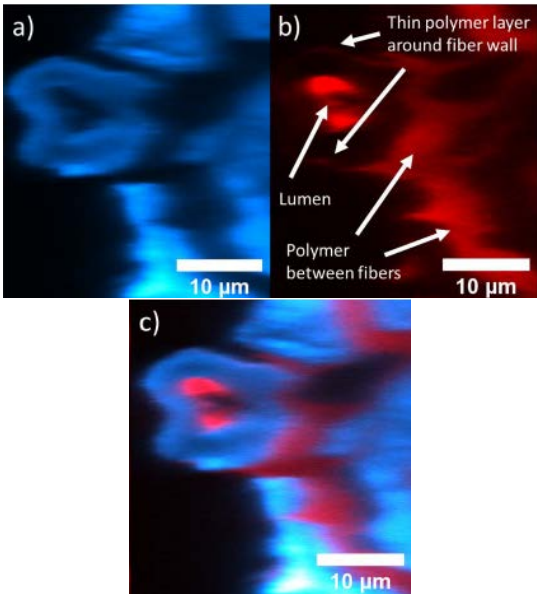

Fig. 2: a) CLSM picture of calcofluor white labeled paper fibers. b) CLSM picture of spatial distribution of rhodamine b labeled wet strength agent c) Z-stacking of previous CLSM pictures for a better understanding of spatial distribution of wet strength agent inside the paper. © CPI, IMTEK Univ. of Freiburg

These studies indicate, that the wet strength agent builds a film inside (in the lumen) and around paper fibers. However, it does not allow an understanding about the exact fail mechanism. Therefore, in this project we want to investigate the exact mechanism of breaking to get a better understanding of the mechanism of wet strength.

Further investigations will focus on reversible surface modification reactions which will ultimately lead to wet strengthened papers that can also be recycled.

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Development of new crosslinker using polymer analogous reactions and re

Johan Liotier[1,2], Jürgen Rühe[1,2]

[1]Department of Microsystems Engineering (IMTEK), Laboratory for Chemistry & Physics of Interfaces, Albert-Ludwigs-Universität Freiburg, Georges-Köhler-Allee 103, 79110 Freiburg, Germany; [2]Cluster of Excellence livMatS @ FIT – Freiburg Center for Interactive Materials and Bioinspired Technologies, University of Freiburg, Georges-Köhler-Allee 105, 79110 Freiburg, Germany

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Hardening polymers is a crucial step to create long lasting materials while keeping them lightweight. This can be achieved on a molecular level via the formation of a 3D network based on covalent bonds via crosslinking.[1]

However, crosslinking often requires catalysts, specific types of chemical functions or monomers and the process is usually irreversible.[2] The goal of this project is to create a universal crosslinker and investigate new ways for cleaving crosslinked networks when they reached the end of their life time.

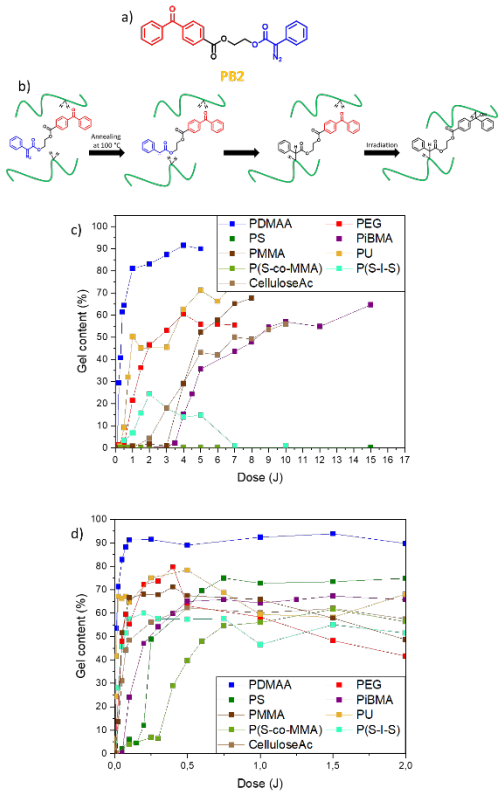

Fig. 1: a) Molecular structure of PB2; b) Crosslinking mechanism with **PB2**; Comparison between the crosslinking behaviors of the nine functionalized polymers at 365 nm (c) and 254 nm (d). (© CPI, IMTEK Univ. of Freiburg.)

To create an universal crosslinker, we got inspiration from our previous work on C,H-insertion crosslinking (CHiC). In that sense, we already intensively studied photoactivated and thermally activated crosslinkers. We aimed at a system containing two moieties that are able to undergo C,H-insertion reaction which have orthogonal activation. The system we designed is orthogonal in the sense that these moieties are activated by different triggers, namely heat and light. We chose to use a diazo compound as thermally activated unit and an aromatic ketone as photoactivated unit. The diazo compound we chose is the PEDAz moiety as it has a low activation energy, as it is able to react at 100°C in 8 hours.[3] This low activation temperature is interesting because it allows for the use of labile polymers that might get degraded at higher temperatures. On the other hand, the photoactive ketone we chose is the BP moiety as it reacts upon UV irradiation but is thermally inert.[4] This gives rises to the molecular structure of **PB2** (Fig. 1a).

The modification procedure used to test **PB2** was designed to be universal and could easily be used for any polymer. The polymer and 5 mol% of **PB2** were dissolved in DCM (2 mL), placed in a vial and vortexed several minutes to have a homogeneous solution. The DCM was then evaporated under reduced pressure at low temperature (40 °C) leaving behind a film at the bottom of the vial. The vial was then closed and heated at 100 °C for 18h. The modified polymers can then be applied on surfaces as thin films and then crosslinked with UV light (Fig. 1b).

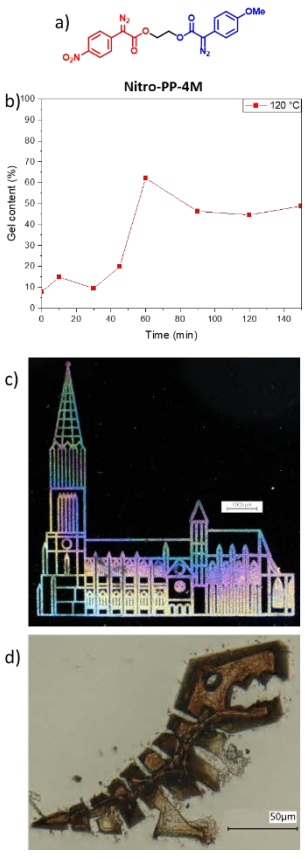

Fig. 2: a) Molecular structure of **Nitro-PP-4M**; b) Crosslinking of a modified PDMAA with **Nitro-PP-4M** at 120 °C; c) Photolittography of a modified PU with **Nitro-PP-4M**; d) Printed dinosaur made with 2 photon lithography from modified lignin. (© CPI, IMTEK Univ. of Freiburg.)

As a demonstration, nine polymers (including acetylated cellulose (CelluloseAc) and polyurethane (PU)) were investigated. These polymes were all successfully modified with **PB2** and could then be crosslinked at 365 nm (Fig. 1c) and 254 nm (Fig. 1d).

To proceed further, another crosslinker based on two PEDAz derivatives was synthesized.[5] This new molecule, **Nitro-PP-4M** (Fig 2a), allowed a much larger use after polymer modification (following the same procedure as described earlier) as it is suitable for thermal crosslinking, photolithography and 2-photon lithography (Fig. 2b, 2c and 2d).

Additionally, to create cleavable networks, a new crosslinker based on MABP with a cleavable unit was synthesized: MA-DA-BP (Fig. 3a). This cleavable unit has been based on a Diels Alder adduct that can be cleaved with temperature.[6,7]

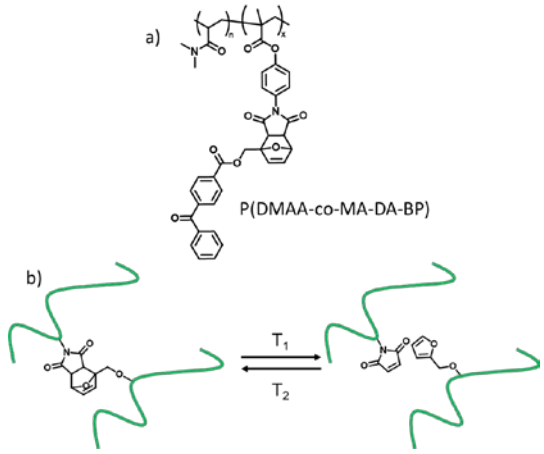

Fig. 3: a) Molecular structure of P(DMMA-co-MA-DA-BP); b) Reversible crosslinking behavior of MA-DA-BP. (© CPI, IMTEK Univ. of Freiburg.)

This type of moiety has been chosen as it is known to be cleavable at a temperature around 120 °C without catalyst, making it an easily recyclable network. In addition, it is, in theory, possible to restore the crosslinked state at lower temperature. This crosslinker already yielded to good results with a full decrosslinking but will be further investigated in the next months.

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Mimicking Synovial Joints: Achieving Superlubricity with Surface-Attached Hydrogels and Water-Soluble Polymers

R. Maraula[1,2], J. Rühe[1,2]

[1]Laboratory for Chemistry & Physics of Interfaces, Department of Microsystems Engineering (IMTEK), University of Freiburg, Freiburg, 79110, Germany; [2]Cluster of Excellence *liv*MatS @ FIT – Freiburg Center for Interactive Materials and Bioinspired Technologies

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The annual toll of high friction and wear is substantial, amounting to a staggering 100 TJ of energy consumption and an alarming 8120 Mt of carbon dioxide emissions.[1,2] Faced with this environmental predicament, there arises a priority to turn towards lubrication solutions that are not only effective but also environmentally friendly. Traditional oil-based lubricants, while undeniably efficient, present challenges in terms of recycling and environmental safety. Responding to this critical need, the focus of this project delves into the promising realm of surface-attached hydrogels, drawing inspiration from the biomechanics observed in synovial joints, proposing them as a sustainable alternative for mitigating friction.[3]

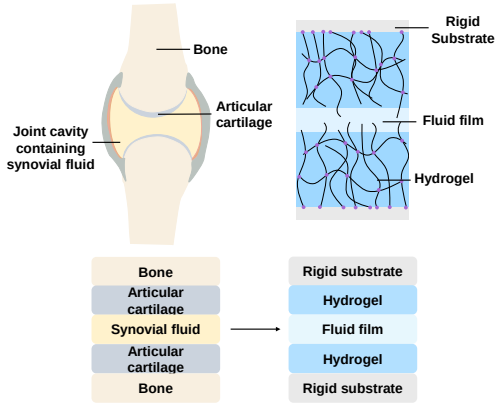

Fig. 7: Analogy of the natural system, the synovial joint, with the technical system, surface-attached hydrogels in Gemini contact. © CPI, IMTEK Univ. of Freiburg.

Hydrogels in self-mated contact (or *Gemini* contact), in their exploration, exhibit solid phases that mimic the elastic properties inherent in cartilage (Fig. 7). When two identical hydrogels come into contact, interpenetration of polymeric chains would result in a critical loss of entropy. This leads to an entropic barrier or steric repulsion, preventing entanglements and interpenetration. As a result, when pressed together, hydrogels exhibit low adhesion, maintaining a film between them with reduced polymer density. Simultaneously, their liquid phases are comprised of water and water-based lubricants, echoing the composition of synovial fluid.[4–6] The focal element of our study revolves around a detailed evaluation of a hydrogel system that utilizes a copolymer of N,N-dimethylacrylamide (DMAA) and methacryloxybenzophenone (MABP) moieties. This unique hydrogel is crafted through the innovative C-H insertion crosslinking (CHic) reaction, elevating its significance in the pursuit of sustainable friction reduction (Fig. 8).[7]

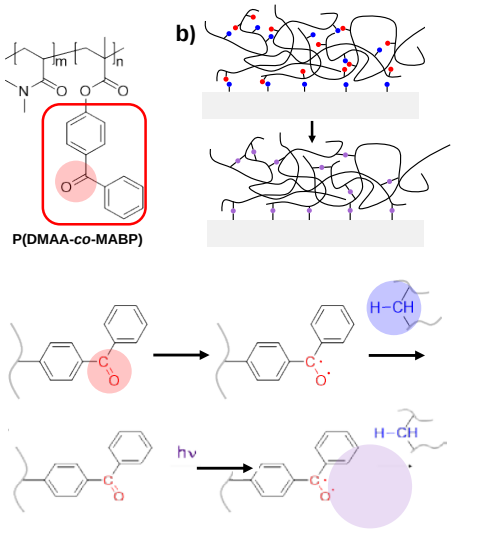

Fig. 8: a) Molecular structure of poly(dimethylacrylamide-co-methacryloxybenzophenone). b) Surface-attachment and hydrogel formation via CHic. c) Reaction mechanism of C-H insertion crosslinking (CHic). © CPI, IMTEK Univ. of Freiburg.

Achieving superlubricity (μ<0.01) is a noteworthy outcome of our investigation, realized through the strategic incorporation of water-based linear polymers such as polyethylene glycol (PEG) and polyacrylamide (PAM). These polymers, with their shear thinning and anisotropic viscosity properties, contribute significantly to the reduction of friction.[8]

Effective friction reduction hinges on crucial factors, namely the absence of entanglements, which highly increase the viscosity of

the polymer solution, and the enhanced stiffness of polymer chains, which might lead to a better alignment under shear. It is imperative, however, to strike a balance where enhanced stiffness does not compromise the water solubility of the system.

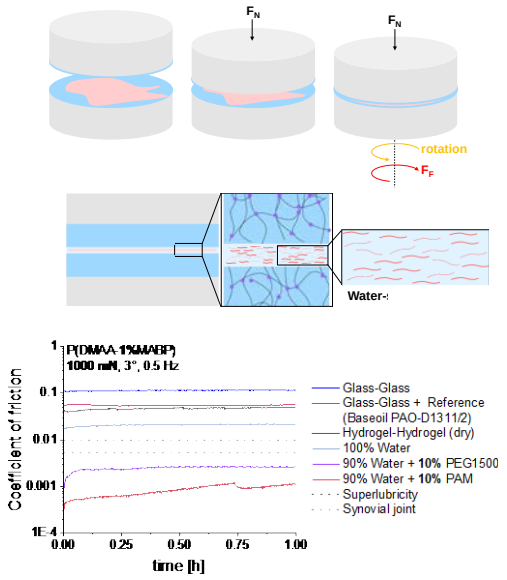

Fig. 9: a) Schematic depiction of rotational measurements between two hydrogel-coated glass lenses (Radius 3.180 mm) with the use of water-based lubricants. b) Schematic depiction of sheared fluid film and model for thin-film lubrication with linear water-soluble polymer. c) Coefficient of friction versus time for different pairs (lens-lens): glass-glass, glass-glass with a reference oil (PAO), hydrogel-hydrogel of P(DMAA-1%MABP) in dry state, and with three water media (100% water, 90% water + 10% PEG1500, and 90% water + 10% PAM). © CPI, IMTEK Univ. of Freiburg.

Incorporating 10% polyacrylamide (PAM, M_n>10000 g mol^{-1}, renowned for its remarkable stiffness in comparison to polyethylene glycol (PEG, M_n=1500 g mol^{-1}), yielded an impressive and durable coefficient of friction of approximately 0.001 at 1000 mN (pressure higher than 20 MPa) between two hydrogel-coated glass lenses in *Gemini* contact. Compared to the dry contact, a reduction of friction of around 99% is achieved. This underscores the potential of these hydrogels as exceptionally efficient lubricants.

Beyond the realm of friction, these surface-attached hydrogels outshine oil-based lubricants by not only showcasing superior friction reduction but also by aligning with the escalating demand for environmentally sustainable solutions. The outcomes of this research firmly position these hydrogels as promising contenders in shaping the landscape of next-generation lubrication technologies. In doing so, they offer a greener and more efficient alternative to conventional oil-based lubricants, catering to the evolving needs of a conscientious and environmentally aware society.

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FUTURE FIELD "BIOMIMETIC, BIOBASED AND BIOACTIVE MATERIALS SYSTEMS"

Climbing plant tendrils as inspiration for soft robotics

Frederike Klimm[1-3], Thomas Speck[1-3]

[1]Plant Biomechanics Group (PBG) Freiburg @ Botanic Garden of the University of Freiburg; [2]Cluster of Excellence *liv*MatS @ FIT – Freiburg Center for Interactive Materials and Bioinspired Technologies; [3]Freiburg Materials Research Center (FMF)

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Despite their sessile nature, climbing plants do move a lot. Their movements differ fundamentally from animal movements though, for example by the absence of localized joints with gliding parts, the absence of a central control unit or by the capability to move by growing. This makes plants promising models for a new group of soft machines and soft robots [1]. Climbing plant movement is particularly pronounced in plant tendrils, which are long, filamentous organs used by climbing plants such as the passion flower *Passiflora caerulea* to attach to support structures. The tendrils anchor by coiling around the support, 'grasping' it. Subsequently, the tendrils coil along their own axis, forming a spring-like structure and shortening, thus hoisting the plant closer to its substrate [2]. Tendril coiling is driven by a difference in length between the tendrils' (prospective) inside and outside [e.g. 3].

We analyzed the arrangement of mechanical tissues in tendrils of various climbing plant species in detail (see Fig. 1). In some plant species, the mechanical tissues are arranged bilateral symmetrically, in form of a band on one side of the tendril. In others, the mechanical tissues are arranged more rotationally symmetric in a core region. However, during development of these plant tendrils, tissue maturation (i.e. lignification) starts on one side of the tendril cross-section [2]. This means that a bilateral symmetric tissue arrangement appears as a transient developmental stage during ontogeny, namely during the coiling phase. The subsequent lignification and thus stiffening of the entire tendril core (Figs. 1A&2A) further stabilizes the coiled shape.

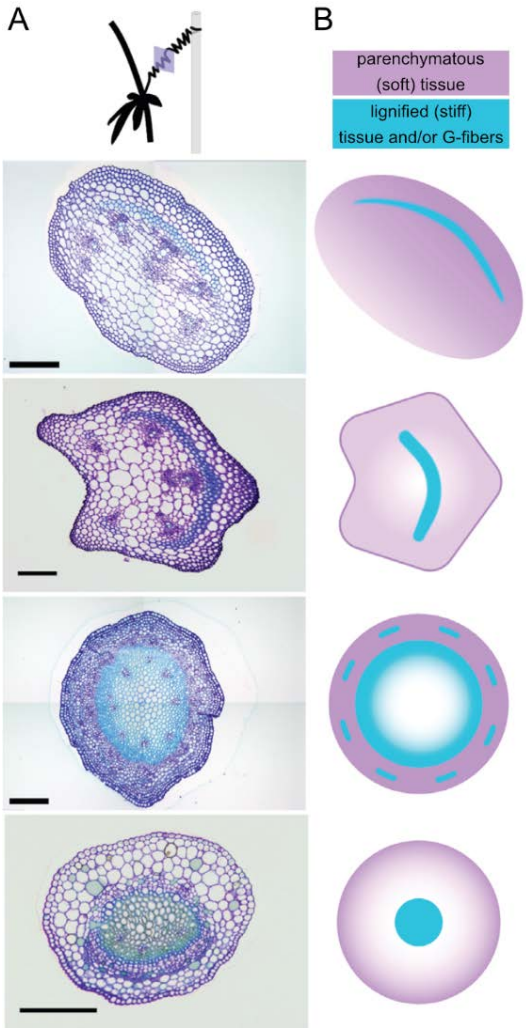

Fig. 1: Tissue organization in climbing plant tendrils. Toluidine-blue stained cross-sections show the anatomy of coiled tendrils of *Bryonia alba*, *Cyclanthera brachystachya*, *Passiflora caerulea* and *Passiflora discophora* (top to bottom) (A). Schematic drawings highlight the tissue arrangement of mechanical tissues (G-fibers and/or lignified tissues) within the parenchyma (B). Scale bars in (A) 200 µm. Figure adapted from [4].

Previous studies have shown the common appearance of a specialized type of fiber cells in tendrils, so called G-fibers, which contract [e.g. 5]. The observed arrangement of mechanical tissues (Fig. 1A), possibly including G-fibers, suggests a straightforward way for inducing coiling by a contractile region positioned on the "inside-to-be" (later concave

side) of the tendril. In cooperation with colleagues from the Helmholtz-Zentrum Hereon, we thoroughly analyzed this coiling principle of plant tendrils for biomimetic abstraction and transfer. As a result, novel bioinspired multimaterial fibers (MMF) mimicking plant tendrils were developed (Fig. 2) [4].

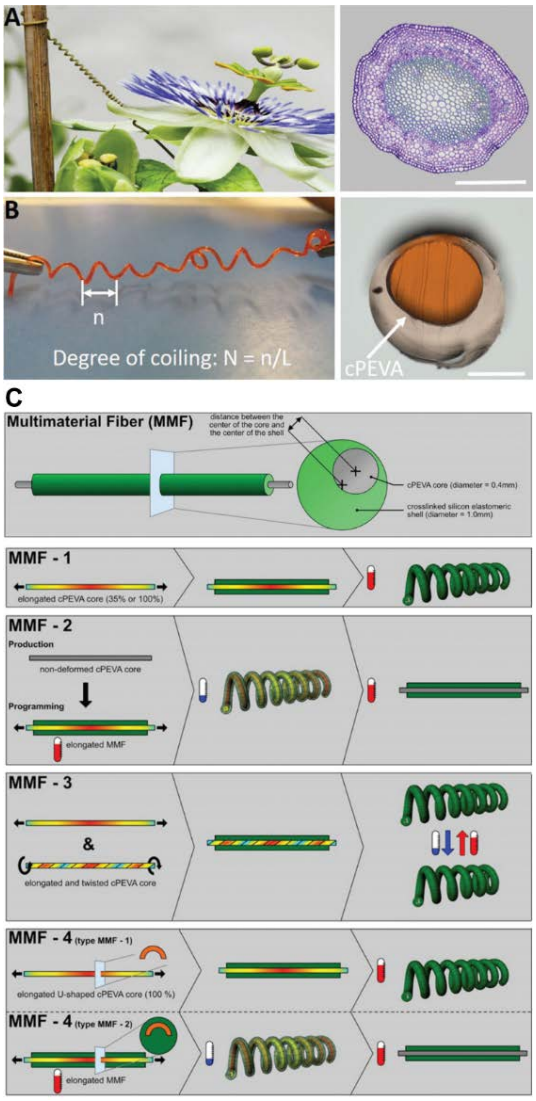

Fig. 2: Artificial multimaterial fibers mimicking plant tendril movements. *P. caerulea* tendril attaching a plant stem with flower to a support, with toluidine-blue-stained cross-section of the coiled tendril (A). Artificial tendril fabricated from a shape-memory-core fiber (cPEVA) surrounded by a cross-linked silicone elastomeric shell, which coils similarly to the plant tendrils based on a strain mismatch between core and shell (B). Several different designs of artificial tendrils developed, achieving not only coiling but also for example uncoiling behavior or a reversible change in number of coils (C). Scale bars in (A) & (B) 400 µm. Figure adapted from [4].

The artificial tendrils are core-shell multimaterial fibers (MMFs), composed of a shape-memory core fiber made of crosslinked poly(ethylene-*co*-vinyl acetate (cPEVA) and an elastic silicone shell (Fig. 2 B&C). Using the shape-memory effect of the core fiber, a strain-mismatch is implemented in the artificial tendrils. In the initial design (MMF-1), the artificial tendril coils when the shape-memory core fiber contracts upon a heat trigger, thus mimicking the contraction of eccentrically arranged plant tissues. Beyond this design, several MMFs were developed that for example uncoil upon a heat trigger (MMF-2) or reversibly change their number of coils (MMF-3).

The observed principle of a stiffening process following the plant tendril movement phase was successfully implemented in an artificial tendril developed by Meder et al. in another project of GrowBot [6]. This tendril coils due to a strain mismatch between a pre-stretched and a relaxed silicone layer and can thereby grasp rod-like supports. Due to an embedded thermoplastic element, the tendril stiffness can be varied by a change in temperature. We have already started to carry out joint experiments with Meder and colleagues to compare artificial and real plant tendrils.

These two examples nicely show the potential of plants as role models for the development for new artificial soft robotic devices. Artificial tendrils could be applied for instance as actuating and support elements for plant inspired growing robots, similar in function to plant tendrils.

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Grown to matter DELIVER project @ FIT

Stefan Conrad[1], Philipp Auth[1], Tom Masselter[1], Thomas Speck[1,2]

[1]Plant Biomechanics Group (PBG) Freiburg @ Botanic Garden of the University of Freiburg; [2]Cluster of Excellence *liv*MatS @ FIT – Freiburg Center for Interactive Materials and Bioinspired Technologies

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In DELIVER, scientists from the Freiburg Clusters of Excellence livMatS and CIBSS and from the Leibniz Institute for New Materials in Saarbrücken (INM) are developping sustainable wood-based materials. The materials are based on microorganisms that produce proteins and can use them to combine wood waste into biocomposites. In the three subprojects of DELIVER groups from synthetic biology, biomimetcs/materials research and machine learning cooperate.

The DELIVER subproject on biomimetics and materials characterization at the Freiburg Center for Interactive Materials and Bioinspired Technologies (FIT) is part of this collaboration between the three work groups. The project focuses on researching sustainable, wood-based materials with precisely controllable properties. The Plant Biomechanics Freiburg is responsible for post-processing material samples, characterizing them structrally and mechanically by using various methods, and for consolidating the data.

In the first year of the projects customised hardware and software have been introduced and integrated to achieve increasingly automated test mechanical procedures. Key achievements include the implementation of a CNC milling machine, a high speed 3D printer, and the addition of a sample wheel and a camera to the existing testing machine. These additions have greatly simplified and sped up the processing and analysis of samples of wood-based materials.

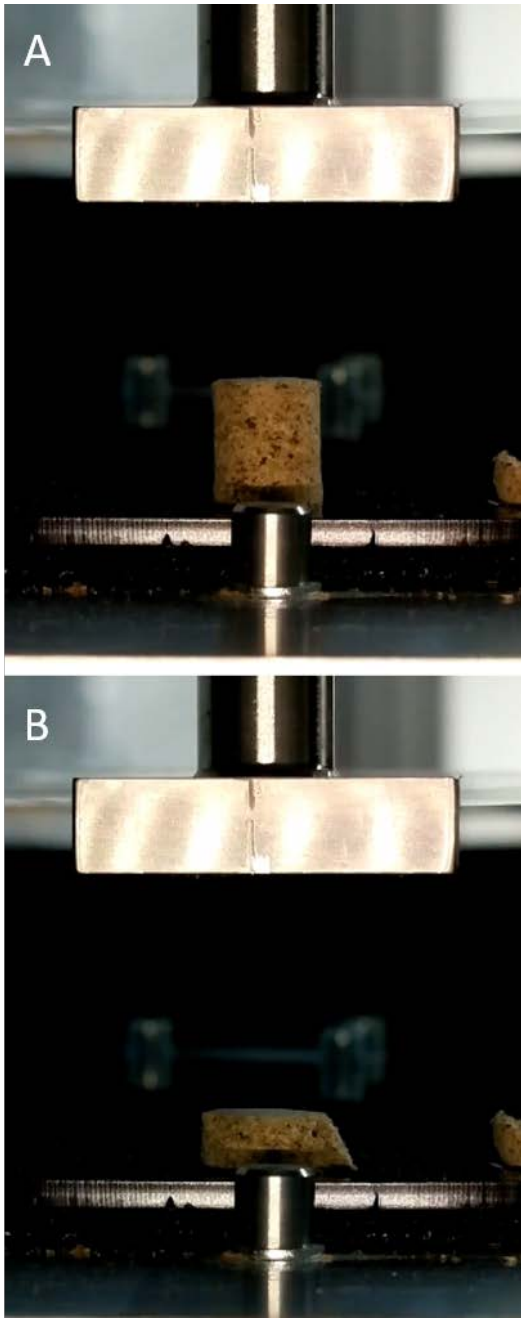

Fig. 1: Automated compression tests of a specimen provided by the sample wheel. (A) Intact sample. (B) Destroyed (compressed) sample. (c) Plant Biomechanics Group Freiburg

Considerable progress has been made in the specimen post-processing through the use of the CNC milling machine to smoothen the

sample surfaces and adjust their geometry. The machine allows up to six specimen to be processed simultaneously and provides a quick manual sample exchange.

For the mechanical characterization, we have developed a compression test procedure (see figure 1). The samples are automatically loaded onto the universal testing machine using a sample wheel that can hold up to 40 specimens. Each compression process is recorded on video and saved for later analysis, which helps to improve our understanding of the material failure.

Post-processing and testing of the specimen are managed by two independent software programs developed within our work group. The BacBoard-Master controls the milling and any potential post-processing steps. It receives the form parameters from a conditions file and selects the milling pattern accordingly. The Samplewheel-Master receives the IDs of the test specimen and matches the generated data before uploading it to the project's shared server for statistical analysis.

One of the main achievements this year has been establishing a strong correlation between compression and material properties. The failure strength has proven to be a good indicator for the prediction of density and Young's modulus and we are confident to identify more related characteristics in the future. However, the project encountered challenges in terms of replication and variability across experiments. To address this, we have set goals in close cooperation with our project partners to automate the specimen fabrication and improve the control of the biochemical components.

Despite these challenges, the DELIVER project remains at the forefront of the integration of synthetic biology, material sciences, and data science. The project's vision of creating sustainable materials in an efficient and cost-effective manner remains our guiding principle. Looking ahead, our focus will be on refining fabrication processes, resolving replication challenges, post-processes and testing.

Developmental process of floating leaves of *Nymphaea caerulea*

Michelle Modert[1,2], Rahel Eckert[1,2], Tom Masselter[1], Thomas Speck[1,2]

[1]Plant Biomechanics Group (PBG) Freiburg @ Botanic Garden of the University of Freiburg;
[2]Cluster of Excellence *liv*MatS @ FIT – Freiburg Center for Interactive Materials and Bioinspired Technologies

Project funding: This work is funded by the Luxembourg National Research Fund (FNR) (15648035).

Among aquatic plants, waterlilies (Nymphaeaceae) are probably the most well-known species. They develop peltate floating leaves that have a long petiole attaching the lamina to the rizhome under water. The lamina can have an orbicular shape, e.g. *Victoria amazonica* and *Euryale ferox* [1, 2], or can have lobed ends, e.g. several *Nymphaea* and *Nuphar* species [3]. In addition, the size can vary between species, ranging from several centimeters to 2-3 metres in diameter in case of *Victoria amazonica* [4, 5].

The developmental process of floating leaves partly takes place under water [2, 4]. We examined this process and related anatomical changes for *Nymphaea caerulea*, which will be described hereafter. First, the leaf emerges from the rizhome, being folded and only a few millimetres long (Fig. 1A).

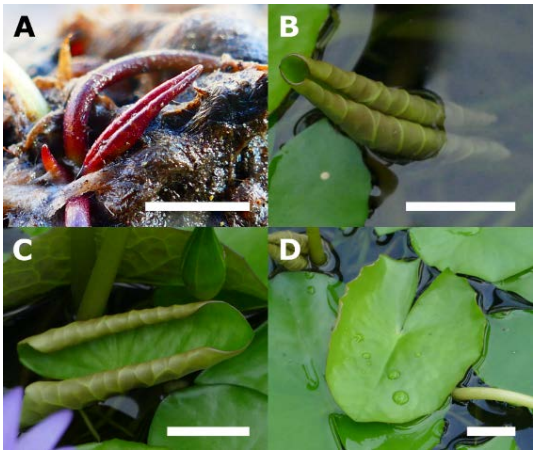

Fig. 1: Development and unfolding process of *Nhymphea caerulea* leaves. Leaf emerging from the underwater rhizome (A), leaf breaking the water surface (B), leaf unfolding at the water surface (C), unfolded adult leaf floating on the water (D). Scale bars = 0,5 cm in (A) and 2 cm in (B-D). © Plant Biomechanics Group

Due to rapid growth of the petiole, the leaf reaches the water surface during in folded stage. Being still entirely folded, the leaf emerges from the water surface (Fig. 1B). Only then the leaf starts to unfold its lamina (Fig. 1C). Younger leaves usually unfold on top of older ones (Fig. 1D), probably to assure continuous photosynthetic activity.

When emerging from the rhizome, the leaf cells are undifferentiated. Afterwards, the aerenchyma, a tissue with wide intercellular spaces, begins to form on the abaxial (= lower) side during underwater leaf stages. When reaching the water surface (prior to unfolding), the leaf tissues are fully developed (Fig. 2).

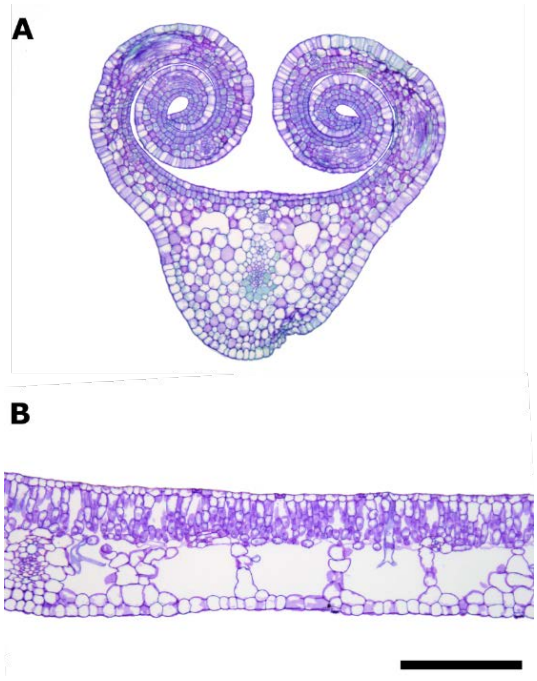

Fig. 2: Changes in anatomy of *N. caerulea* leaves during development Start of tissue differentiation in juvenile, folded leaves (A), mature tissue with parenchyma and aerenchyma in adult, fully unfolded leaves (B). Scale bar = 200 µm for (A) and (B). © Plant Biomechanics Group

The unfolding process of *N. caerulea* leaves resembles other floating leaves such as *Euryale ferox* or *V. amazonica*. In all these species unfolding starts on top of the water surface by simultaneous opening of the two leaf halves [2, 4].

The anatomical structure is highly similar in all floating leaves, with aerenchyma tissue situated on the abaxial side that grants buoyancy as well as aeration in the petioles [3, 6].

In addition to the here described analyses of the developmental processes during unfolding of floating leaves of *Nymphaea caerulea* in this project also unfolding processes of other plant species with peltate leaves are studied, as e.g. *Syngonium podophyllum* and *Pilea peperomioides* [7]. The studies on functional morphology and biomechanics during the unfolding process serve to compare different airborne and floating peltate leaves with the ultimate aim of developing bioinspired folding and unfolding processes for packing and unpacking thin technical foil structures.

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Delamination robustness and resilience in cone scales of *Pinus jeffreyi*

Kim Ulrich[1,2], Tom Masselter[1], Thomas Speck[1,2]

[1]Plant Biomechanics Group (PBG) Freiburg @ Botanic Garden of the University of Freiburg; [2]Cluster of Excellence *liv*MatS @ FIT – Freiburg Center for Interactive Materials and Bioinspired Technologies

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Passive hygroscopic plant movements such as the opening mechanism of pine cones were the inspiration for the passive and energy-autonomous façade shading system "SolarGate", an interdisciplinary collaborative project of the Plant Biomechanics Group Freiburg and the Cluster of Excellence "Living, Adaptive and Energy-autonomous Materials Systems (livMatS)" at the University of Freiburg with the "Cluster of Excellence Integrative Computational Design and Construction for Architecture (IntCDC)" at the University of Stuttgart. Since the long-term usability of these 3D-printed façade shading demonstrators may be limited due to possible delamination of the hygroscopic active layer and the resistance layer [1], we aim for a better understanding the robustness and resilience of pine cone scales against cyclic actuation and possible delamination.

Pine cone scales bend due to the anisotropic elongation of their tissues along the longitudinal axis under varying ambient humidity. The different angles of the cellulose microfibrils in the cell walls of the sclereid layer and the sclerenchyma fibres determine the extent of longitudinal elongation due to changes in ambient humidity [2]. Hygroscopic bending of cone scales can even be observed in 15 million years old fossil specimens [3]. Early descriptions of the pine cone scale system compared its operating principle to that of a bimetallic strip [4]. Recent studies have highlighted the complexity of the scale system by underlining the importance of the brown tissue as an intermediate layer between the sclereid cells and the sclerenchyma fibres [5], the role of the epidermis in water uptake [6] and the hetero-structured spring/square microtubes in the sclerenchyma fibres [7].

Fig. 1: Six cone scales of *Pinus jeffreyi* are mounted in the pine cone submerger. During our experimental timeline each scale completed 102 cycles of actuation. During each cycle they were first submerged in water for 90 min and then dried in front of a fan for 4,5 h. (© Plant Biomechanics Group)

As a first step towards a better understanding of the pine cone scale system, we conducted a series of experiments with separated pine cone scales of Pinus jeffreyi to investigate whether they can maintain their functionality under multiple cyclic actuations. For this purpose, the dimensions and weight of the scales were documented and the scales were visualised with two micro-CT scans, the first before and the second after a blocking force measurement of each scale. These scales were then mounted in an automated pine cone submerger (Fig. 1), which allowed us to achieve four opening and closing movements per day, resulting in a total of 102 cycles for each scale. The scales were then visualised a third time using a micro-CT scanner and the blocking force was measured again. The opening angle of the scales was observed during the 102 cycles. Through this series of experiments, we were able to demonstrate the sustained functionality of the scales, even in the presence of extensive delamination between the sclerenchyma fibres and the brown tissue [8].

The next step will be a more detailed analysis of the humidity dependent swelling and shrinking of pine cone scale tissue samples at the microscopic level using nano-CT visualisation under different ambient humidity conditions and precise (de-)sorption measurements. The

resulting information about the anisotropic swelling and shrinking behaviour can then be used to simulate the pine cone scale with its different tissues in order to better understand which structural parameters or gradients affect the resistance and resilience of the pine cone scales and to what extent.

In addition to the work on the pine cone scales, we have also characterised the curvature of the current SolarGate actuators as a function of relative humidity at different ambient temperatures (Fig. 2). The aim is to better understand the temperature dependence of the demonstrators and to obtain a benchmark of the functionality and limitations of the current demonstrators, in order to later work on improving their robustness and resilience based on the insights gained from our work with the pine cone scales.

Fig. 2: Ten 3D-printed hygroscopic actuators were mounted in a climate chamber for an experimental series of five temperature steps ranging from 10 to 50°C. For each temperature step, the relative humidity was systematically increased from 15% to 95%. During this series of experiments, the curvature of the demonstrators was calculated using a custom-made tracking tool and three markers (numbered points, e.g. 25-27) on the outer edge of each specimen. (© Plant Biomechanics Group)

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3D printed pneumatic logic for the control of soft walking robots

Joscha Teichmann[1,2], Falk Tauber[1,2], Thomas Speck[1,2]

[1]Plant Biomechanics Group (PBG) Freiburg @ Botanic Garden of the University of Freiburg; [2]Cluster of Excellence *liv*MatS @ FIT – Freiburg Center for Interactive Materials and Bioinspired Technologies

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Robots, widely used in modern industries, perform diverse tasks like lifting and manipulating. Initially only designed for dangerous or monotonous work, millions are now globally deployed. Traditional robots, with rigid materials and electric actuators, dominate, despite complex control mechanisms. Soft robots, unlike traditional 'hard' robots, mimic nature's soft systems. Inspired by organisms like cephalopods and vertebrates, they feature continuously deformable structures and muscle-like actuators, adapt to confined spaces, manipulate objects with unconventional geometries,

and operate without intricate control [1, 2]. This simplicity yields streamlined control, enhanced robustness, and lower costs, as compliant robots' joints don't need motors, gears, or roller bearings. Additionally, they often use leg-based mobile platforms, eliminating the need for traditional propulsion systems [2].

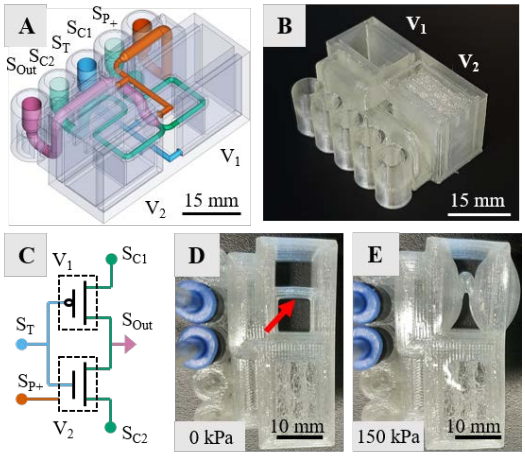

Fig. 1: Soft pneumatic logic gate. A: Model of the pneumatic logic gate (PLG) consisting of two soft valves V_1 and V_2. Two input channels S_{C1} and S_{C2} (green) lead through one valve each and merge in the output channel S_{Out} (pink). S_{P+} (orange) connects the lateral chambers of V_2 to a constant pressure supply, thereby kinking the tube of S_{c2} by default. A high signal at S_T (blue) switches the conductivity of the valves by closing V_1 and opening V_2. B: 3D printed PLG made of TPU A 70 using fused deposition modeling. C: Schematic CMOS diagram showing that S_T switches the conductivity of S_{Out}, connecting either S_{C1} or S_{C2} [17]. D: Atmospheric pressure at S_T creates a pneumatic equilibrium at the membranes, so that the tube (red arrow) is conductive. E: Overpressure of 150 kPa at S_T makes the membranes of the lateral chambers expand, thereby kinking the tube inside the central chamber. Adapted with permission by Springer-Verlag from [4].

To tackle the issue of controlling compliant robots without relying on rigid electronics, we have developed soft, pneumatic logic gates (PLGs). These gates offer an easy and cost-effective solution and can be 3D printed using common FDM printers in just several hours [3]. Once printed, these modules are ready for use and can withstand high pressures of up to 400 kPa. Additionally, their modular design allows for versatility. They comprise of two sets of pneumatic chambers and tubes forming soft valves mimicking electronic transistors (Fig. 1 A, B). The antagonistic interplay of normally open and normally closed soft valves enables the PLG to function like an electronic Schmitt trigger. In our pneumatic rendition, an overpressure signal at the shared socket S_T switches the output socket S_{Out} from connecting to input channel one to being linked to input channel two (Fig. 1 C). In a pneumatic equilibrium, membranes within the valves are relaxed (Fig. 1 D). However, applying a HIGH signal as overpressure to the lateral chambers causes expansion, kinking a tube in the central chamber to inhibit airflow (Fig. 1 E). When the lateral chambers are consistently pressurized, applying the signal to the central chamber unkinks the tube, allowing airflow to resume [3].

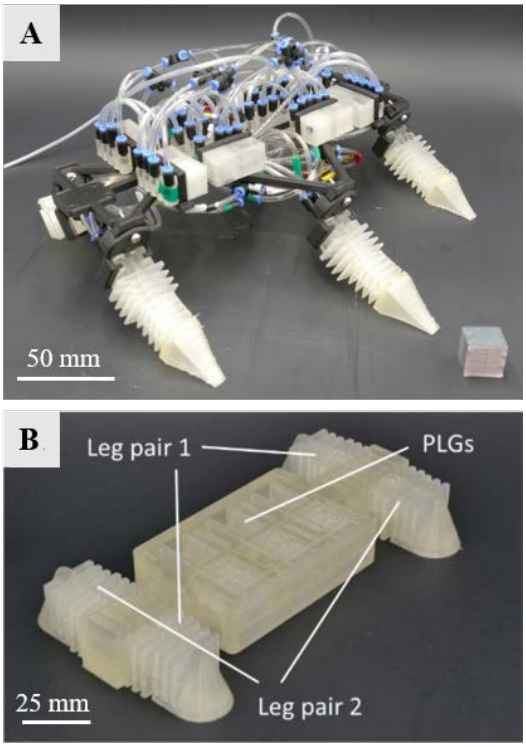

Fig. 2: Soft robotic walkers controlled by PLGs. A: Stick insect inspired compliant robot featuring six insect inspred leg actuators on a rigid frame controlled by 8 PLGs to achieve forward locomotion. Adapted with permission by Springer-Verlag from [4] B: Soft walker printed in one process on an FDM printer with an integrated oscillator of three PLGs [3].

Current soft logic modules have efficient designs, allowing them to function as a single-valve oscillator or as a button [5]. However, they have low material durability and require either manual casting and intricate assembly [5, 6], or rely on less accessible polyjet 3D printing technology with manual removal of support material [7]. The next steps will be to reduce the size of the PLG and create more integrated circuits that are ready to operate from the printbed, without the need for assembly.

To demonstrate how our logic gates are able to replace electrical control circuits, we built a fully pneumatic drink dispensing system, a biomimetic hexapodal soft-legged walker inspired by the stick insect *Carausius morosus* (Fig. 2 A), and also integrated a minimal three PLG oscillator circuit into a four-legged fully soft robotic walker (Fig. 2 B).

At 225 kPa system pressure, the six-legged walker moves at a speed of 61 mm/s requiring an airflow around 10.07 l_n/min [4]. Its gait allows a statically defined stand at all times by standing on three legs at once and waiting to lift one group of three legs until the other group has established ground contact. The integrated four-legged walker was printed in one continuous process and walks with a speed of 33 mm/s at 175 kPa system pressure in a trot-like gait [3]. In a series of resilience tests it even withstood being run over by a car. Both robots are able to operate untethered with a CO_2 cartridge and a pressure regulator. Our developed systems enable the construction of complex autonomous robots that are entirely free of electronics. These robots can be utilized in areas where electricity is compromised by environmental factors or in search and rescue operations where it may be compromised.

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Bio-inspiration for pneumatic finger actuators with variable stiffness: The avian tendon locking mechanism

Peter Kappel[1,2], Lukas Kürner[1,2], Thomas Speck[1,2], Falk Tauber[1,2]

[1]Plant Biomechanics Group (PBG) Freiburg, @ Botanic Garden of the University of Freiburg; [2]Cluster of Excellence *liv*MatS @ FIT – Freiburg Center for Interactive Materials and Bioinspired Technologies

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In the "Demonstrators" research area of the Cluster of Excellence livMatS, our efforts are dedicated to the exploration of devices suitable for showcasing practical applications of living materials systems. Our research exploits the vast potential of biology to integrate life-like properties into materials systems, such as adaptability and autonomy. When it comes to tangible demonstrators for technical application but also for public outreach, macroscopic robots are well suited, and bio-inspired soft robots in particular stand out for their intrinsic softness and compliant properties. As a real-world demonstrator, we are researching soft robotic grippers as a platform to explore the elastic motions found in animals and plants to achieve adaptability.

Manipulation of the environment and interacttion with objects are fundamental aspects of both living organisms and technological systems. In nature, organisms have evolved a great variety of grippers, appendages, and

specialized structures to engage with their surroundings, showcasing a remarkable level of adaptability to diverse environments and objects. This ability to manipulate and interact with objects is equally crucial in the realm of technology, where robots and robotic systems play pivotal roles in various applications. Adaptation becomes a key factor, especially when objects in an unknown environment can have a wide range of properties. Soft robotics, as an emerging field, seeks innovative strategies to imbue robots with the flexibility and adaptability observed in nature.

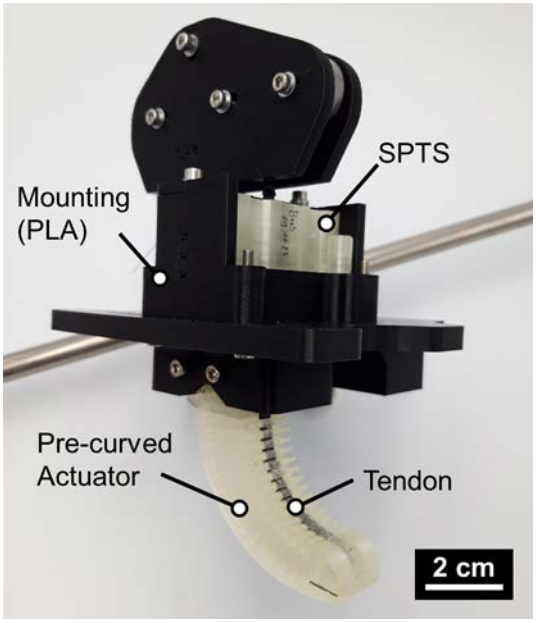

Fig. 10: The pneumatic actuator system with avian-inspired tendon locking mechanism (TLM). (© Plant Biomechanics Group)

One such strategy involves the development of grippers capable of altering their own properties, such as form and stiffness, to suit different tasks and objects. The actuators we have developed are a promising step in this direction, offering the ability to dynamically change stiffness. This ability to adapt is a key feature in developing grippers that can seamlessly adapt to the characteristics of different objects, making them highly versatile in unpredictable environments. Moreover, the ability to modulate stiffness brings benefits for autonomous robots, as reducing stiffness during actuation concurrently decreases the actuation energy required to operate the actuator and gripper, paving the way for more energy-efficient and sustainable robotic systems.

The aim of this research was to create a pneumatic bending actuator system that can adjust its stiffness and operate with reduced air pressure [1]. The inspiration for this system was the avian tendon locking mechanism (TLM), which represents a remarkable adaptation found in many bird species [2]. This mechanism enables the flexion of digits with minimal energy expenditure during actions such as perching on tree branches or grasping prey. The stiffness-changing properties described earlier were implemented using state-of-the-art 3D printing [3]. The three main parts of the TLM actuator system were printed from TPU A70, a flexible filament with high tensile strength beneficial to fabricate soft pneumatic actuators [4]. While conventional pneumatic network actuators (PNAs) require constant pressure for sustained operation, such as bending and force generation [5], our design relies on an inversely working pre-curved PNAs. The pre-curved bending actuator straightens during actuation and bends when actuation stops. This is due to the geometry of the actuator, which results in low structural stiffness in the direction of straightening. Bending occurs as a result of the relaxation of the deformed flexible material, allowing for the low operating pressure (Fig. 1). The other two parts of the actuator system are a soft pneumatic tendon sheath (SPTS) and a flexible tendon. The blocking of the tendon in the SPTS channel during bending modifies the stiffness of the actuator. The SPTS is a second actuator that expands when pressurized, allowing the tendon to pass through, and relaxes when depressurized, blocking the movement of the tendon. The system was characterized using a comprehensive analysis that measured key parameters such as SPTS channel opening distance, actuator bending angle, and block force versus applied air pressure. The results indicate that the system can generate a substantial maximum block force (~4.6 N) while operated with low air pressure. The pre-curved actuator was found to operate at a pressure of ~60 kPa, while the SPTS operates at 160 kPa. This has the potential to further reduce the operating pressure for the entire system to 60 kPa or to increase the block force while maintaining the higher operating pressure. This underscores its potential for use in

autonomous soft robots that have limited onboard energy resources. Moreover, the use of a tendon within the presented actuator system showed good form adaptability and can contribute to the system's ability to adapt to objects and handle them without the need for external sensors, simplifying the overall design and enhancing the system's practicality. In conclusion, the fusion of nature-inspired designs with advanced fabrication techniques contributes to the ongoing evolution of soft robotics, paving the way for more efficient, adaptable, and responsive robotic systems.

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Digital image correlation-based deformation measurements of water submerged samples

Max Mylo[1,2], Kaiyang Yin[1,2], Premnath Srinivasan[1,2], Chris Eberl[1,2]

[1]Cluster of Excellence *liv*MatS @ FIT – Freiburg Center for Interactive Materials and Bioinspired Technologies; [2]Chair of Micro and Materials Mechanics, Department of Microsystems, University of Freiburg, Freiburg, Germany

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Digital Image Correlation (DIC) is a powerful technique in experimental mechanics for non-contact measurement of full-field displacement and strain fields on the surfaces of structures. Operating by comparing digital images of an object at different times or under varying loading conditions, DIC identifies subsets of pixels and tracks their movement over time using image correlation algorithms, enabling the calculation of strain fields. Rooted in the mid-1800s field of photogrammetry, DIC saw significant development in the 1980s with the rise of digital cameras and has since found applications in various fields, undergoing improvements in accuracy, speed, and robustness. Its advantages include being non-contact, non-invasive, and having no temporal resolution limitations [1]. The technique accommodates both time-lapse recordings of slow movements [2] and high-speed recordings of rapid events [3], with spatial resolution ranging from the nanoscale to the macroscale.

DIC is not restricted to conventional digital cameras and can be applied to various imaging devices, including light microscopes, infrared cameras, electron microscopes, and 3D imaging methods like CT and MRI. There are two main types of DIC: 2D-DIC for planar surfaces and 3D-DIC (stereo-DIC) for non-planar surfaces or out-of-plane deformations (Fig. 1A&B). 3D-DIC involves a calibration step to establish a relationship between digital images and physical dimensions, requiring a calibration target with distinctive markers. Stereo cameras with synchronized image capture and a stereo angle of approximately 20-30°

are used for 3D-DIC, and the calibration information is crucial for accurate displacement and deformation determination.

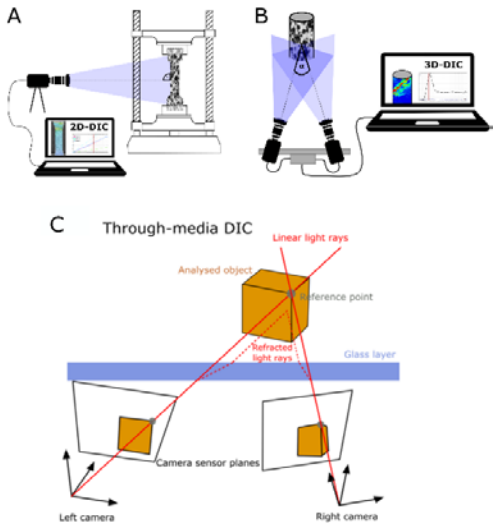

Fig. 1: Schematic representation of digital image correlation setups. **A**: Example of a single camera setup for measuring flat samples under tensile load. **B**: Example of a stereo camera system for the analysis of uneven samples or out-of-plane motion. **C**: DIC measurements through glass (also at air-water transitions) lead to measurement errors due to inaccurate calibration of the system because of refraction of the optical rays. These must be compensated for to allow measurements of samples submerged in water or in climatic chambers. **A&B** from [4], **C** © IMTEK Freiburg.

DIC analysis involves correlating image series from one or two cameras covering the undeformed and deformed states of the sample. Small areas or subsets serve as basic units for correlation analysis, with the correlation process involving shifting and deforming subsets between images. Displacement vectors are obtained for each subset, and strain fields are calculated from these vectors. The process is repeated for all subsets across the region of interest, producing a displacement vector map. The method allows for detailed analysis and quantification of individual points and sections, providing valuable data for material characterization, structural comparison, and finite element simulations. The DIC workflow encompasses sample and setup preparation, image correlation, and data analysis, allowing for the visualization and quantification of surface movement or deformation patterns over time.

In recent years, DIC has become increasingly recognised in plant research and offers unique opportunities to characterise a wide variety of biological and bioinspired materials systems [4]. A notable limitation in standard DIC techniques, particularly during 3D-DIC calibrations, arises when assessing hygroscopically influenced materials underwater. Most DIC software assume linear optical paths, causing challenges in measuring through glass or observing samples submerged in water due to different refractive indices (Fig. 1C). To address this issue, the research group of Chris Eberl at IMTEK acquired a commercial software capable of correcting for non-linear optical paths. Subsequently, a student project successfully implemented the concept of non-linear corrections into an existing open-source 3D-DIC code. This advancement proves particularly valuable for measurements involving air-water transitions, such as the dynamic closure of pine cone scales when dry samples are placed in water. The implemented code was compared with the commercial software, revealing similar measurement accuracy. This showcases the potential of the method and opens the door for future enhancements, including corrections for measurements through multiple layers of glass. Such improvements would facilitate deformation analyses in environmental chambers, allowing the characterization of hygroscopically responsive samples under defined temperature and humidity conditions.

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FUTURE FIELD "(MICRO)SYSTEMS FOR ENERGY CONVERSION, STORAGE AND ENERGY-AUTONOMY"

Carbon black supported Ag nanoparticles in zero-gap CO_2 electrolysis to CO enabling high mass activity

Khaled Seteiz[1,2], Josephine N. Häberlein[1,2], Philipp A. Heizmann[1,2], Joey Disch[1,2], Severin Vierrath[1,2]

[1]Freiburg Center for Interactive Materials and Bioinspired Technologies (FIT); [2]Electrochemical Energy Systems Group, IMTEK - Department of Microsystems Engineering, University of Freiburg

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To achieve global net-zero CO2 emission targets, we must defossilize all sectors that rely on carbon energy and fossil feedstock. The electrochemical reduction of CO2 is a very promising approach to defossilize the chemical industry and create a closed carbon loop. This technology enables the production of chemical feedstocks using captured CO2, water, and renewable energy. The simplest product of electrochemical CO2 reduction is CO, which is a widely used feedstock in a wide range of industrial processes. A zero-gap electrolyzer is a common design for electrochemical CO2 reduction. In this setup, the CO2 reduction catalyst is deposited onto a gas diffusion medium to form the so-called gas diffusion electrode (GDE). During operation the GDE is fed with humidified CO2, which is being reduced at the catalyst in the presence of water, forming CO and hydroxide anions. These anions migrate form the cathode to the anode side and are oxidized to form oxygen [1].

Metal-based catalysts such as copper, gold, silver, and zinc are most commonly used to facilitate this reduction reaction. Besides catalytic activity also the selectivity plays a key role, especially towards the strongly competing hydrogen evolution reaction. Among these metal-based catalysts, Au has the highest selectivity for the production of CO, followed by Ag, Cu, and Zn [2,3]. However, due to the high price of Au, Ag is the most commonly employed catalyst material.

To become more cost-effective, the required amount of catalyst can be reduced by supporting the catalyst on a cheap support material like carbon particles. Furthermore, the support introduces an additional degree of freedom in the design, e.g. to ensure that reaction sites are well dispersed [4]. Figure 1 shows the TEM micrographs of three different synthesized carbon black supported Ag nanoparticles.

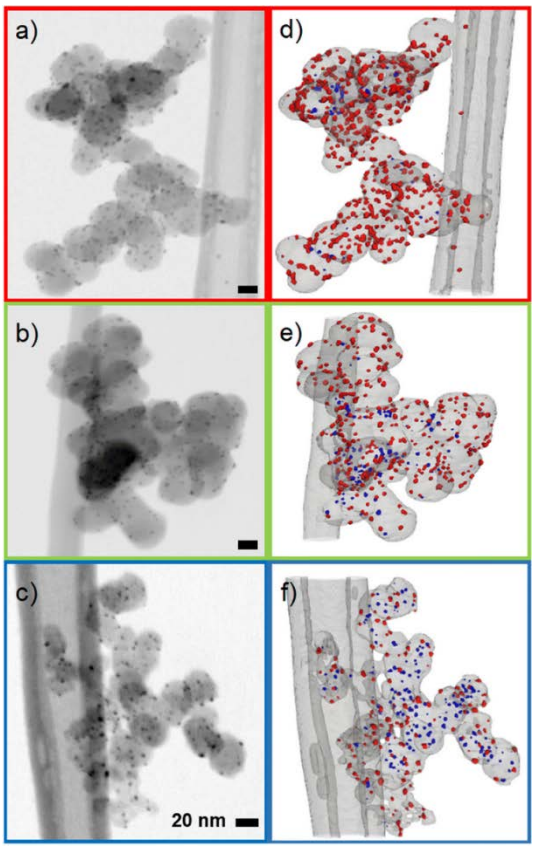

Fig. 1: Electron tomography of Ag particles supported on three carbon blacks: Ag on Super P (red), Ag on Vulcan (green), Ag on Ketjenblack (blue). (a–c): Representative Bright Field Scanning Transmission Electron Micrographs (BF STEM) of the Ag/C samples. (d–f): Segmented volumes showing interior (blue) and exterior Ag nanoparticles (red). Note that the segmented volumes contain depth and thus the 2D *vs.* 3D projections do not match exactly in this representation. (adapted from Seteiz *et al.* [4] CC BY Copyright © 2023)

For the three carbon substrates shown, spherical Ag nanoparticles are homogeneously distributed over the entire carbon support surface. The average nanoparticle diameter was found to be 5 nm, which is believed to be the

optimal particle size towards CO formation [5]. Figure 2 demonstrates the electrochemical performances in the zero-gap electrolyzer.

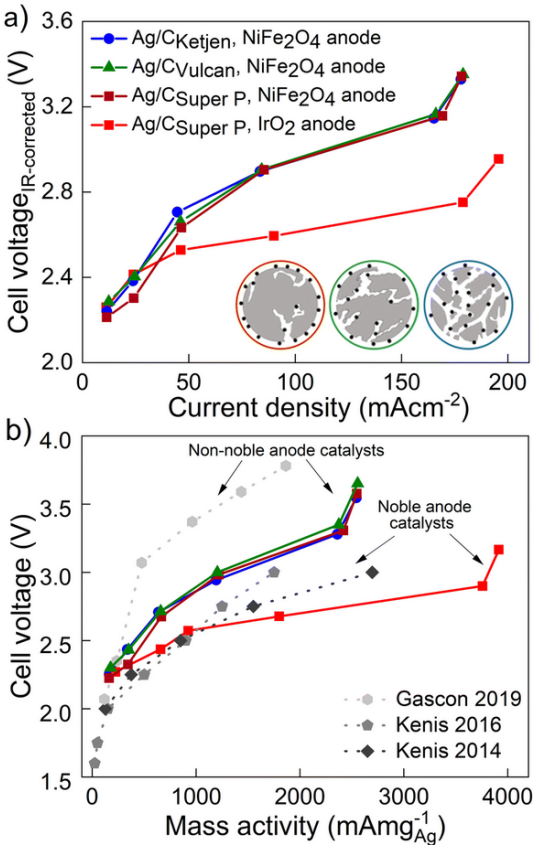

Fig. 2: (a) *iR*-Corrected cell voltage over CO partial current density for Ag/C$_{Ketjen}$, Ag/C$_{Vulcan}$ and Ag/C$_{Super\ P}$ catalysts in 0.1 M KOH at ambient temperature. (b) CO partial current density relative to Ag loading of selected supported Ag catalysts achieving high mass activities. (adapted from Seteiz *et al.* [4] CC BY Copyright © 2023)

The synthesized Ag/C catalysts demonstrate high mass activities amongst reported literature for carbon supported Ag catalysts. There is no significant trend in performance when comparing the three different carbon supports, despite the significant differences in surface area (from 50 to 800 m2g−1) and localization of the Ag particles on the support. This is a strong indicator that the peak performance and the mass activity are not limited by the catalyst kinetics but by mass transport limitations similarly affecting all three supported catalysts. This further means that the catalyst support surface area does not play a role in the investigated systems, which used PTFE (non-ion conducting) as an electrode binder.

In future research, we consider employing an anion-conductive electrode binder, which might be atvantageous, especially as water consumption rises at high current densities. In that case, the surface area of the carbon could emerge as a crucial factor for the cell performance.

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A Comprehensive Measurement System for Measuring ZT and Contact Resistance of Vertical Thermolegs

Negin Sherkat[1], Athira K. Sivaparasad[1,2], Uwe Pelz[1,2], Peter Woias[1,2]

[1]Laboratory for the Design of Microsystems, Department of Microsystems Engineering (IMTEK), University of Freiburg; [2]Cluster of Excellence livMatS @ FIT – Freiburg Center for Interactive Materials and Bioinspired Technologies, University of Freiburg

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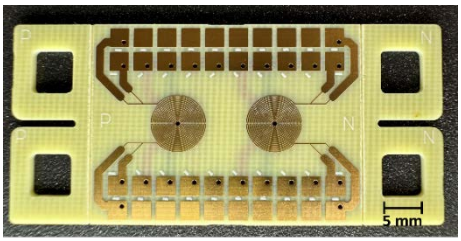
The exploration of energy harvesting technologies has experienced significant growth in recent years due to the escalating demand for compact, lightweight, and energy-autonomous

devices. These devices capture and transform ambient energy from diverse environmental sources into usable electrical energy. Commonly utilized energy harvesting devices encompass solar panels, wind turbines, thermoelectric generators, and RF harvesters [1]. They contribute to harnessing energy that would otherwise be wasted, offering a sustainable and renewable power source for diverse applications.

(a)



(b)

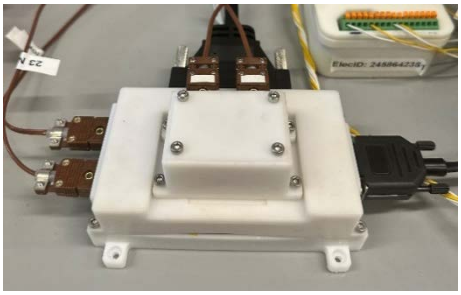


Fig. 1: (a) Top view of the ZT-Card PCB (b) Overview of the setup for the measurement platform which consists of thermocouples, thermocouple holders, spring contacts, DSub connectors and the ZT-Card. © IMTEK/Laboratory for Design of Microsystems

Micro-thermoelectric generators (µTEGs) represent a subset of energy harvesting devices that convert temperature differentials into electricity through the Seebeck effect [1]. Temperature gradients for these devices can be derived from various sources, such as industrial processes, vehicle engines, or human body heat. µTEGs possess several advantages, including compact size, absence of moving parts, noise-free operation, no greenhouse gas emissions and long-term operational capability [3]. These attributes render µTEGs suitable for a wide array of applications, such as energy harvesting for wireless sensor nodes (WSNs), wearable electronics, remote sensing systems, and many more.

The limitation of µTEGs is at the same time one of their advantages: their small size. This reslts in (generally) lower conversion efficiencies than larger-scale thermoelectric systems and over all lower power outputs compared to alternative harvesting technologies [2].

In order to still maximize µTEG efficiency, high quality thermoelectric (TE) materials are required for its fabrication. [2]. The performance of a thermoelectric material can be measured by its dimensionless figure of merit (ZT), which depends on its Seebeck coefficient, electrical conductivity and thermal conductivity. Improving ZT is critical for optimizing thermoelectric materials, but measuring it in a µTEG configuration poses significant challenges.

This work outlines the development of an integrated ZT-Card measurement platform (Fig. 1a) for the comprehensive thermal and electrical characterization of thermoelectric materials [3]. The process involved the optimization, simulation and testing of a spiral microheater for creating a temperature gradient along the thermoelectric material for Seebeck voltage measurements. A 3D printed housing/ platform (Fig. 1b and Fig. 2) was developed to accommodate spring contacts for electrical measurements, thermocouples for Seebeck measurements and connectors for interfacing with the Keithley instrumentation. A user-friendly GUI was developed using Python programming to streamline measurements and communication with the Keithley instrumentation.

The ZT-Card was tested with n-type Bi2Te2.7Se0.3 and p-type Bi0.5Sb1.5Te3 thermoelectric materials. The Seebeck coefficient for the n-type material was measured to be -98 µVK-1 ± 12.8 µVK-1, and for the p-type material, it was 205 µVK-1 ± 26.5 µVK-1, aligning closely with values reported in literature. Both materials showed a fairly high electrical resistance of 0.355 Ω and 0.323 Ω for a single leg of n- and p-type materials respectively and therefore a relatively low electrical conductivity (14.07 Scm-1 for n-type and 15.27 Scm-1 for the p-type). Transfer length measurements (contact resistance between TE material and Cu contacts) within the ZT-Card unveiled elevated contact resistance values ranging from 83 mΩ to 670 mΩ. The observed lower electrical conductivity was at-

tributed to the higher contact resistance measured, sometimes caused by limited contact between the thermoelectric material and the copper ring in the bottom layer after hot pressing. The preliminary thermal conductivity values, obtained via a transient hot bridge (THB) setup using the squares on both sides of the ZT Card (Fig. 1 a), were 0.42 Wm-1K-1 for the n-type material and 0.23 Wm-1K-1 for the p-type material. The highest ZT values observed could be calculated to be 0.012 for the n-type material and 0.094 for the p-type material.

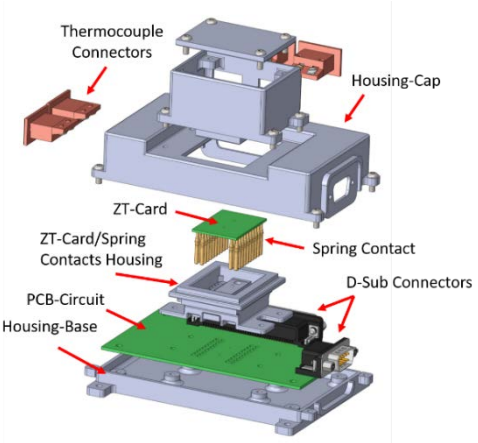


Fig. 2: Exploded view of the measurement housing platform. © IMTEK/Laboratory for Design of Microsystems

In summary, the project could successfully demonstrate the ZT-Card's capability to accurately conduct electrical conductivity, contact resistance and Seebeck voltage measurements in order to ultimately obtain the ZT value of thermoelectric materials.

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Guiding Transient Peptide Materials with Structural Elements around Phosphate Fuels

Mahesh Pol, Kun Dai and Charalampos G. Pappas

Cluster of Excellence livMatS @ FIT – Freiburg Center for Interactive Materials and Bioinspired Technologies

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Biochemical phosphates activate specific tasks by incorporating structural and recognition elements in their chemical structure.1 Adenosine triphosphate (ATP) powers motor proteins, while guanosine triphosphate (GTP) orthogonally activates microtubule assembly. The triphosphate region in these structures reduces the propensity towards hydrolysis, while the nucleoside region enables selective binding of biocatalysts. In addition to phosphoric anhydrides, biology has chosen various other phosphate-containing molecules, like creatine or carbamoyl phosphate to drive diverse metabolic processes - thus demonstrating its ability to accommodate structural diversity. This structural variation in turn, enables the activation of specific biological functions without any interference. Biochemical phosphates have inspired chemists to move from traditional systems which function under thermodynamic control, to chemical reaction networks, where kinetic effects and non-equilibrium pathways become important. Thus, biotic phosphates have been used in the form of ATP (as a signal or as a co-assembling molecule) or DNA strands to drive non-equilibrium processes. Some of these strategies utilize amino acid residues featuring hydroxyl groups, which can in turn be employed to access supramolecular assemblies via phosphorylation and de-phosphorylation cycles. Despite the great progress on the construction of chemically driven assemblies, currently, most approaches do not consider the structure of the fuel as a critical element to control the processes. Current strategies mainly focus on variations in the chemical structure of the substrates to tune the formation of supramolecular assemblies.

The discovery of fuels, capable of incorporating structural and recognition elements in their structure remains challenging.[1] The reason that remains challenging is associated with stability of activated molecules in different environments and the presence of water which tends to hydrolyze labile intermediates.

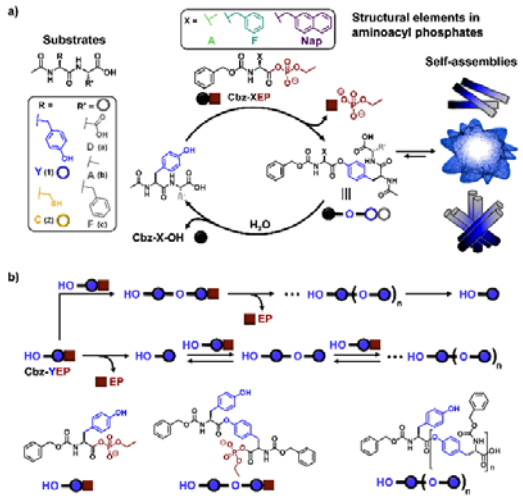

Fig 1: Schematic representation of the construction of transient peptide assemblies from the reaction between Cbz-phosphate esters (Cbz-XEP) and dipeptide substrates: (a) Reaction cycles in the presence of dipeptides. (b) Self-ligation using Cbz-YEP. (@Pappas Research Group)

Inspired by biochemical phosphates, herein we design abiotic phosphates[2] capable of incorporating structural elements in their structure. We demonstrate that the amino acid side chains (A, F, Nap) in the structure of aminoacyl phosphate esters direct the lifetime, the mechanical properties and the structural organization of esters and thioesters upon adding tyrosine or cysteine-containing peptides. Transferring energy and reactivity from the molecularly dissolved acyl phosphates, self-assembly protects the newly formed peptide derivatives from hydrolysis. This process allows for the transient formation of various supramolecular structures, such as fibers, tapes and sunflower-like fibrillar assemblies (Figure 1a). Furthermore, the incorporation of a tyrosine residue (Y) around the phosphate esters leads to autonomous oligomerization and de-oligomerization of esters in one-pot (Figure 1b). Our findings suggest that structured abiotic phosphates can be utilized to guide assembly and induce reactivity changes in the context of non-equilibrium structure formation.

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Development of an evaluation kit for STEM-based tomography data for the investigation of PtCo/C PEMFC electrocatalysts

Philipp A. Heizmann[1,2], Severin Vierrath[1,2], Carolin Klose[2]

[1]Freiburg Center for Interactive Materials and bioinspired Technologies (FIT), University of Freiburg and [2]Electrochemical Energy Systems Group, IMTEK – Department of Microsystems Engineering, University of Freiburg

Project funding: Federal Ministry of Education and Research (BMBF), Project “FC-CAT fuel cell CFD and through-plane modelling”

Parts of the following article have already been published in the peer-reviewed journal *RSC Advances*.[1] For further in-depth information about this study, we kindly refer to this paper.

Proton exchange membrane fuel cells (PEMFCs) emerge as a promising and environmentally friendly technology for various power source applications, particularly in the automotive heavy-duty and energy industries, owing to their high power density, low operating temperature, and rapid refuelling capabilities.[2] Despite their potential, the widespread commercialization of PEMFCs faces a significant hurdle due to their high cost, mainly attributed to the platinum-based electrocatalyst, which constitutes a substantial portion of the overall price. To address this challenge and explore avenues for cost reduction, researchers have investigated Pt*M*/C alloy catalysts, where *M* represents metals such as Co, Fe, and Ni, and C represent porous carbon supports such as

Vulcan XC-72R or Ketjenblack EC300J. These alloy electrocatalysts have demonstrated heightened activity in the oxygen reduction reaction (ORR), leading to notable performance enhancements compared to systems based solely on pure Pt/C. This research seeks to pave the way for more economical and efficient PEMFCs, facilitating their broader adoption in various industries.[3]

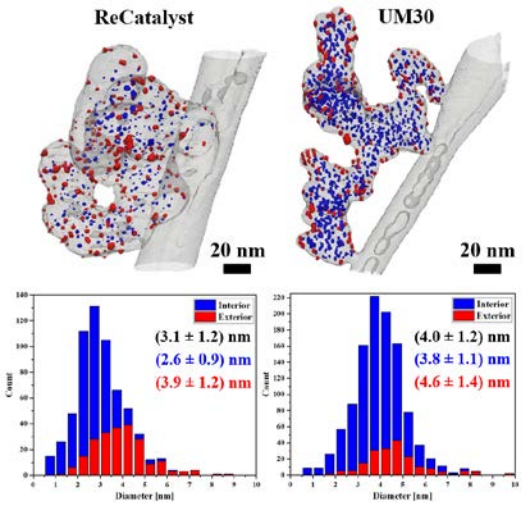

Fig. 1: Segmented volumes of a ReCatalyst (left) and a UM30 PtCo/C particle (right) and corresponding particle size distributions with subdivision of nanoparticles into interior (blue) and exterior (red). (© Electrochemical Energy Systems Group)

The further development of these electrocatalysts requires a deep understanding of the complex interaction between the transport processes of the reactants, the electrochemical reaction and the microstructure of the active layers. A partial aim of 'FC-CAT' thus is to interconnect experimental data with improved fuel cell models to develop a reliable and comprehensive basis for future research.

One of the best characterization methods to investigate the structure, composition and porosity of these novel electrocatalysts and thus to determine structure-activity correlations is the employment of 3D [scanning] transmission electron microscopy ([S]TEM). Recent research suggests that the nanoparticle position might significantly influence the ORR activity.[4] In previous years we therefore established and further developed [S]TEM-based tomography to systematically locate the position of individual Pt- and PtCo nanoparticles, allocating them to be either in the interior or the exterior of the carbon support. This year, we further refined this analysis by including position-dependent volumes and surface areas, along with nanoparticle-specific shape factors such as sphericity, elongation, and flatness. Notably, interparticle distances were incorporated and compared with theoretical approximations for the first time. Details of this development and the favourable side effect that this analysis is applicable to other important electrocatalysts (e.g. Ag/C) can be found in the recently published corresponding doctoral thesis.[5]

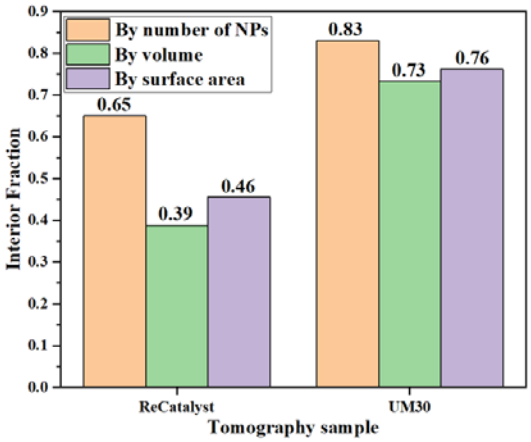

Fig. 2: Interior fraction of nanoparticles regarding their number, their volume and their surface area for the two examined PtCo/C species. (© Electrochemical Energy Systems Group)

To illustrate these developments, Fig. 1 displays the reconstructed volumes and the particle size distributions of two investigated PtCo/C species: one is a state-of-the-art commercial electrocatalyst from Umicore NV/SA (Elyst Pt30 0690, denoted as UM30), and the other is a novel electrocatalyst provided by the collaborating research group led by Dr. Matija Gatalo and Dr. Nejc Hodnik from the National Institute of Chemistry, Ljubljana, Slovenia (denoted as ReCatalyst). From the rendered volumes, it is visually evident that the majority of the nanoparticles for both samples are embedded in the interiors of the respective carbon supports. Although the nanoparticles appear spherical, their shapes deviate slightly, with average sphericities of 0.92 (ReCatalyst) and 0.88 (UM30). Considering nanoparticle sizes (Fig. 2), a noteworthy discovery

emerges: While the interior fraction is dominant by the number of nanoparticles for both samples (65 % for ReCatalyst and 83 % for UM30, respectively), the interior fraction is only dominant for the UM30 species by *surface area* (39 % and 73 %, respectively). This distinction is crucial when explaining differences in observed electrochemical behaviour or implementing experimental data in advanced models.

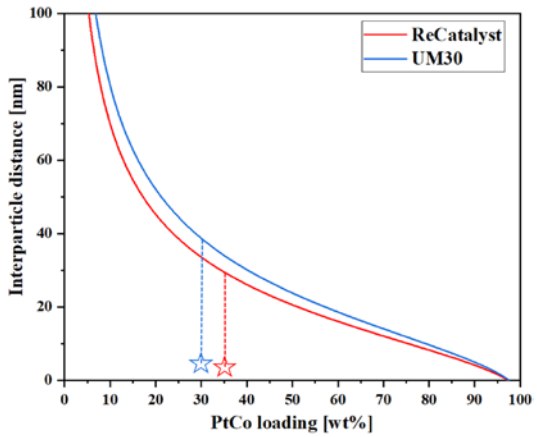

Fig. 3: Calculation of border-to-border interparticle distances via the approach of Meier *et al.*[6] for PtCo nanoparticles using the determined average nanoparticle sizes and assuming densities of ρ_{Pt} = 21.45 g/cm^3 and ρ_{Co} = 8.90 g/cm^3 and a surface area of 800 m^{2}g^{-1} for the carbon support. The hollow stars depict the obtained distances by STEM 3D analysis. (© Electrochemical Energy Systems Group)

Interestingly, the experimental investigation and theoretical approximation of the interparticle distance, believed to have a significant impact on the electrocatalyst stability due to the probability of coalescence increasing with decreased nanoparticle interdistance,6 leads to strongly diverging results: The experimental interparticle distance is significantly lower than predicted (Fig. 3). As both methods are flawed – the theoretical approximation neglects the intrinsic porosity of the carbon support, while the experimental evaluation currently ignores the existence of carbon support-based barriers between nanoparticles –, these approaches have to be improved and corrected, eventually providing approximately the same values.

Thus, while important progress has been made in analysing such electrocatalysts via [S]TEM tomography, there are still important adjustments necessary to enable models and experimental data to converge.

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Structural and electronic properties of a layered halide perovskite for photo-battery applications

Cong Tao[1,2], Wei Wei[1,2], Julian Gebhardt[2], Daniel F. Urban[2,3], and Christian Elsässer[1,2,3]

[1]Cluster of Excellence *liv*MatS @ FIT – Freiburg Center for Interactive Materials and Bioinspired Technologies; [2]Fraunhofer Institute for Mechanics of Materials IWM, Wöhlerstraße 11, 79108 Freiburg, Germany; [3]Freiburg Materials Research Center (FMF), Albert-Ludwigs-Universität Freiburg, Stefan-Meier-Straße 21, 79104 Freiburg, German

Project funding: Funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) under Germany's Excellence Strategy – EXC-2193/1 – 390951807

A SolStore Mode-III photobattery device requires an absorber material with not only a suitable optical band gap but also a good ionic conductivity and lithium storage capacity. To explore potentially suitable photobattary materials, we extend our previous work in livMatS on three-dimensional (3D) halide perovskites to layered halide perovskites with two-dimensional (2D) crystal structures because of their potentially better chemical stability.

In this work, we investigate 2,6-diammonium anthraquinone lead iodide (DAPbI), which has recently been reported in an experimental work [1] to possess both photovoltaic energy conversion and electrochemical energy storage capabilities. Using computational methods of density-functional theory (DFT), we calculate structural and electronic properties with and without interstitial Li ions for the widely studied Dion-Jacobson (DJ) phases in DAPbI, with unshifted (0,0 displacement) and shifted (1/2, 1/2 displacement) mutual stackings of the inorganic layers [2]. Our atomistic structure models are illustrated in Fig. 1.

First, we study the stability of interstitial Li atoms in DAPbI. Taking the (1/2, 1/2) displaced model, we insert a Li atom at two different positions: i) the octahedral void in the inorganic layer, and ii) close to the oxygen atom in the organic spacer. Comparing the formation energies for the inserted Li atom, the energy of the latter case is about 0.95 eV lower than that of the former case, indicating that likely Li atoms are preferentially located in the organic layers of the DAPbI.

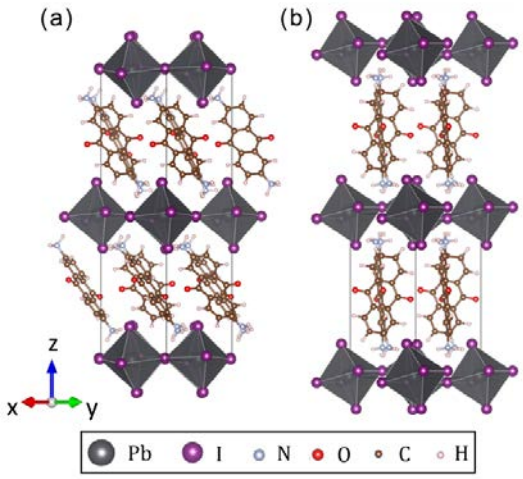

Fig. 1: The atomistic models for the DJ phase in 2,6-diammonium anthraquinone lead iodide (DAPbI) with (a) the (1/2, 1/2) displaced stacking of the inorganic layers and (b) the (0, 0) displaced stacking of the inorganic layers.. © C. Elsässer's Group

Next, we study the electronic structures of DAPbI starting with the (1/2, 1/2) displaced model without Li. For an accurate description of the electronic structure, we applied the DFT+1/2 method to Pb and I, as described in Ref. [3], and to O which is present in the organic molecule DA. This enlarges the sub-band gap of the DA molecule and causes the inorganic elements (Pb & I) to contribute to the valance band edge (see the atom-projected electronic densities of states (DOS) in Figure 2).

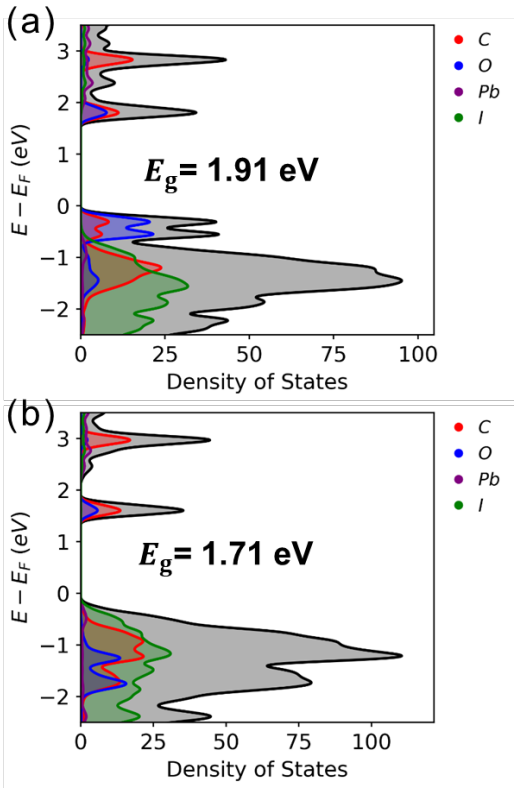

Fig. 2: Electronic DOS for the (1/2, 1/2) displaced model in DAPbI (a) without and (b) with a DFT+1/2 treatment of O ($r_{\mathrm{cut}}^{\mathrm{O}} = 2.8$ bohr). The total DOS is shown in grey while the projected DOS of C, O, Pb, and I are shown in red, blue, indigo, and green, respectively. © C. Elsässer's Group

Using this methodology, we investigate the electronic structures of the Li-containing structures for the two cases described above: The presence of Li reduces the band gap value from 1.71 eV to 1.55 eV and 1.63 eV, respectively, for Li located in the inorganic layer and in the organic spacer, respectively, cf. Figure 3. This reduction is explained by i) the structural changes induced by the intercalated Li atom, and ii) the extra electron provided by the addition of a Li atom.

Overall, the insertion of lithium into the 2D perovskite crystal led to a decrease in the band gap, which is in contradiction to the results obtained for Li_xCsPbI_3 in our previous study on

3D halide perovskites. This decreasing band gap must be taken into account for potential photobattery applications.

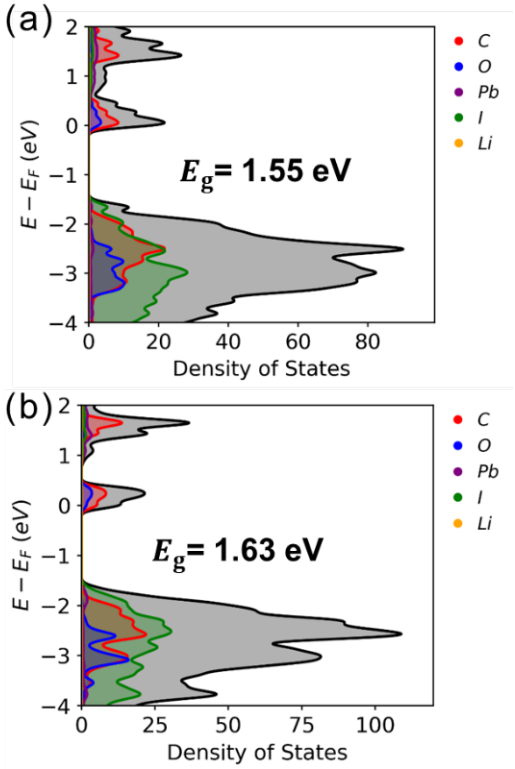

Fig. 3: Electronic DOS for the (1/2, 1/2) displaced model with a Li atom inserted (a) into the inorganic octahedral void; (b) close to the oxygen atom of the inorganic DA spacer. The color code follows Figure 2. There is no substantial Li contribution (orange) visible in the plotted energy range. © C. Elsässer's Group

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Application of In-situ Electrochemical Liquid (Scanning) Transmission Electron Microscopy in understanding Materials Dynamics under Electrochemical Conditions

S. Esmael Balaghi[1,2], Sima Heidari[1,2], Anna Fischer[1,2,3]

[1]Freiburg Center for Interactive Materials and Bioinspired Technologies (FIT), University of Freiburg, Georges-Köhler-Allee 105, 79110 Freiburg, Germany; [2]Freiburg Materials Research Center (FMF), University of Freiburg, Stefan-Meier-Straße 21, 79104 Freiburg, Germany; [3]Institute of Inorganic and Analytical Chemistry (IAAC), University of Freiburg, Albertstraße 21, 79104 Freiburg, Germany.

The project “In-situ EChem-(S)TEM” funded by the Volkswagen Foundation in the Momentum funding scheme is dedicated to studying the dynamics of electrochemical energy conversion and storage materials under operational conditions at the nanoscale using in-situ electrochemical transmission electron microscopy techniques (Figure 1).

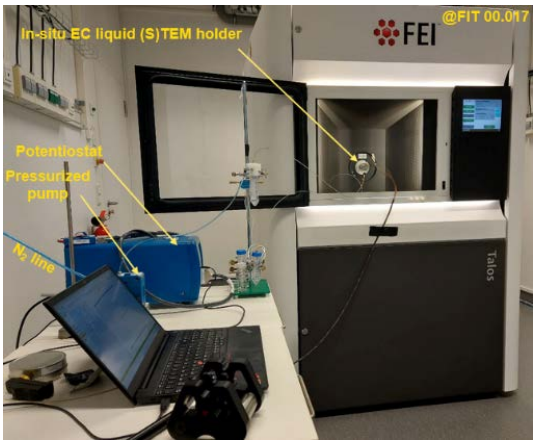

Fig. 1: In-situ Electrochemical Liquid (Scanning) Transmission Electron Microscopy set-up installed and run by the Fischer group at the core facility “Imaging of material systems” at FIT. Image copyright ©AK Fischer. All rights reserved.

Recent advances in the micro-fabrication of electrochemical MEMS devices and their combination with electron microscopy methods have opened new horizons allowing to study the complex and dynamic behavior of electrochemical energy materials at the nanoscale under electrochemical conditions. Materials of

interest are, for example, electrocatalysts for electrochemical energy conversion and fuel cells, as well as battery materials for electrochemical energy storage. The knowledge gained in such in-situ studies will improve the understanding of the materials “under operational condition” and therefore help to pave the way to design and manufacture materials with improved performance in terms of activity, storage capacity, or long-term stability.

In one of the current projects under the Momentum scheme, we applied the in-situ EC TEM techniques to investigate the electrodeposition of ZnSO4 solution into electroplated Zn-based nanostructures, with relevance to the application of Zn ion battery anodes. The morphological evolution of the deposited material was characterized using HAADF-STEM-EDX methods, as presented in Figure 2. Understanding the dynamics of the electrodeposited species on the working electrode can provide valuable insights into the performance and stability of Zinc anodes.

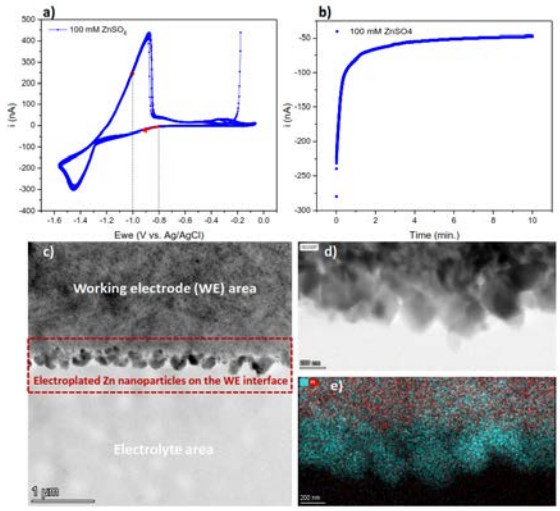

Fig. 2: a) Cyclic voltammogram of a 100 mM $ZnSO_4$ solution in our in-situ electrochemical liquid (S)TEM cell (electrolyte flow rate = 10 µl.min^{-1}; voltage scan rate: 50 mV.s^{-1}). b) Chronoamperometry results showing Zn electrodeposition from a 100 mM $ZnSO_4$ solution in our in-situ electrochemical liquid (S)TEM cell (electrolyte flow rate = 10 µl.min^{-1}; applied voltage: -1.4 V vs. Ag/AgCl). c) TEM image of the working electrode interface during Zn electrodeposition (100 mM $ZnSO_4$). d) HAADF-STEM image and e) HAADF-STEM-EDX analysis of the working electrode interface during Zn electrodeposition (100 mM $ZnSO_4$). Image copyright ©AK Fischer. All rights reserved.

The second major advancement in our in-situ EC (S)TEM setup is the development of custom Python-based scripts, expertly tailored to precisely control and synchronize the setup's integral components. This system consists of three primary data-generating elements: the Transmission Electron Microscope, outfitted with a FEI Ceta camera for capturing image sequences during experiments; the potentiostat, which regulates various electrochemical conditions like scan rate, current, or voltage; and the pumping system, tasked with maintaining specific flow rates or pressures. Effective synchronization of these components is essential for simultaneous image acquisition, potentiostat-driven potential/current profiling, and pumping system flow/pressure monitoring.

Development of SolStore devices to harvest and store electrical energy

Jan Büttner,[1,2,3] Taisiia Berestok,[1,2,3] Rodrigo Delgado Andrès,[1,2,4] Robin Wessling,[1,2,4] Yu Wang,[1,2,3] Maria Belen Camarada,[1,2,3] Sven Porath,[1,2,3] Birgit Esser,[1,2,4,5,] Ingo Krossing[1,2,3,4], Stefan Glunz,[1,2,4,6,7] Uli Würfel,[1,2,4,6] Anna Fischer[1,2,3,4]

[1]Cluster of Excellence livMatS; [2]Freiburg Center for Interactive Materials and Bioinspired Technologies (FIT); [3]Inst. for Inorganic and Analytical Chemistry (IAAC), University of Freiburg; [4]Freiburg Material Research Center (FMF); [5]Inst. for Organic Chemistry (IOC), University of Freiburg; [6]Fraunhofer ISE, Freiburg; [7]Department of Sustainable Systems Engineering (INATECH), University of Freiburg

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The cooperative project *SolStore* aims at the development of highly integrated solar-charging energy devices, such as solar batteries and solar capacitors, able to harvest, convert and store solar energy from their surroundings. To realize such self-charging electrochemical devices with high level of integration, different modes of integration (mode II and mode III) involving either three or two electrodes, respectively, are tackled. In all cases photo-charging electrodes combining the function of energy harvesting and storing in one device (mode II) or material system (mode III) are explored.

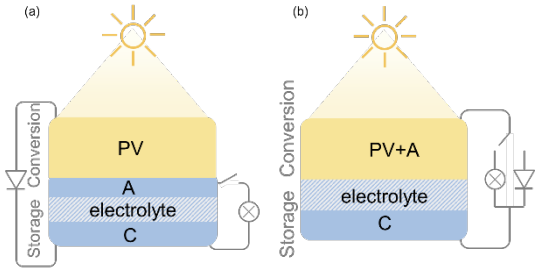

Fig. 1: Schematic diagram of the Mode II (a) and Mode III (b) photostorage devices. © *liv*MatS / Daniel Hellweg

The *SolStore* project combines advanced material development (simulation and synthesis), characterisation and testing along with device fabrication, simulation and optimization; tasks achieved in cooperation in a large team of experts with complementary expertise.

Status-Quo in the development of mode III devices?

For mode III, two types of potentially self-charging photobattery materials systems have been identified at the beginning of the Solstore project: a) donor-acceptor bulk-heterojunctions of tailored conjugated polymers (*Organic Solstore – oSolstore*) and b) inorganic semiconductors with suitable hole- and electron-extraction layers (*Inorganic Solstore - iSolstore*).

However, after several years of research, no mode III material could be developed within the Solstore projects.

In the Organic Solstore project novel bifunctional acceptor-donor conjugated polymers based on phenothiazine as donor and diketopyrroldopyrrol and benzothiadiazole as acceptors were developed, demonstrating either PV absorber or LIB storage functionalities (PI Esser, Würfel). However, a true mode III photobattery functionality involving light induced photocharging could not be demonstrated.[1]

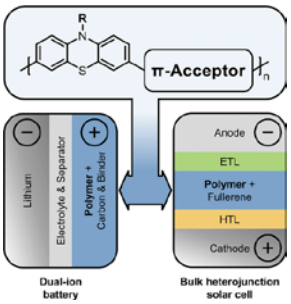

Fig. 2: Bifunctional phenothiazine donor-acceptor conjugated co-polymers with PV or battery functionality. Reproduced from [1]

In the Inorganic Solstore project a previously reported photobattery material based on a 2D lead halide perovskite has been revisited (PI Fischer, Hillebrecht, Krossing).

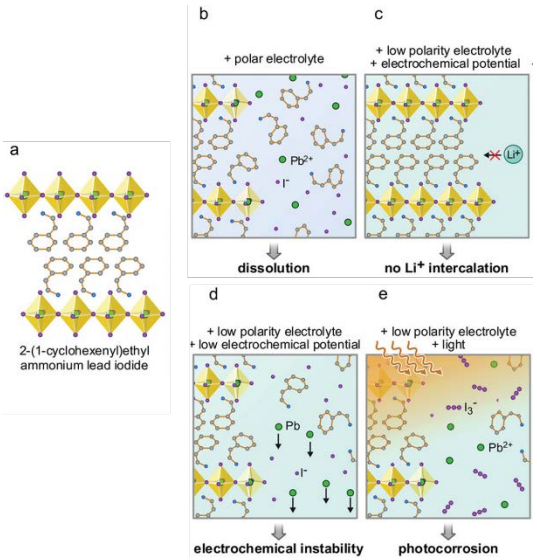

Fig. 3: Schematic of the demonstrated CHPI behaviour for different scenarios. (a) Simplified schematic structure. (b) Dissolution in polar solvents. (c) Stability in low polarity electrolytes, but no quantitative Li^+ intercalation. (d) Reductive electrochemical degradation by Pb^0 formation. (e) Photo corrosion under illumination. Adapted from [2]

The results unambiguously prove that this type of material class is unsuitable for photobatteries as they dissolve in LIB electrolytes and lack a true redox functionality.[2] The in-

vestigation of another perovskite based photobattery material with a true redox functionality based on the organic linker yielded unfortunately similar results.

To conclude, the Solstore projects results strongly indicate that previously published claims on mode III materials are misconceived and rather relate to material instabilities or photo or thermal responses not in pair with any battery functionality. For these reasons, further efforts in the field of photobatteries have been and will be based on mode II devices, while the identification of true mode III materials remains an open challenge.

Status-Quo in the development of mode II devices?

At the beginning of the Solstore projects, a lot of efforts have been invested into the development of mode II photosupercapacitors. Here, perovskite solar cells, silicon solar cells and organic solar cells have been monolithically integrated with mesoporous N-doped carbon-based supercapacitors, yielding highly integrated and functional photosupercapacitors (PI Fischer, Glunz, Würfel). [3, 4, 5] These however are so far restricted to rather low voltages and thus energy densities.

To circumvent these limitations, photobatteries in mode II were and are tackled within the Solstore projects.

Here, photobatteries based on inorganic, organic or organic-inorganic material combinations have been and are currently being developed.

Amongst others a purely organic photobattery integrating a high voltage multi-junction organic solar cell and a stable polymer-based lithium-ion battery, was developed (PI Esser, Würfel, Fischer). [6] The multi-junction organic solar cell is capable of charging up to voltages as high as 4.2 V under varying illumination conditions. The fully organic photobattery demonstrated fast photo-charging within minutes and supplied on-demand discharge capacities of up to 22 mAh/g (regarding battery active material) with average discharge potentials of 3.6 V vs. Li/Li^+.

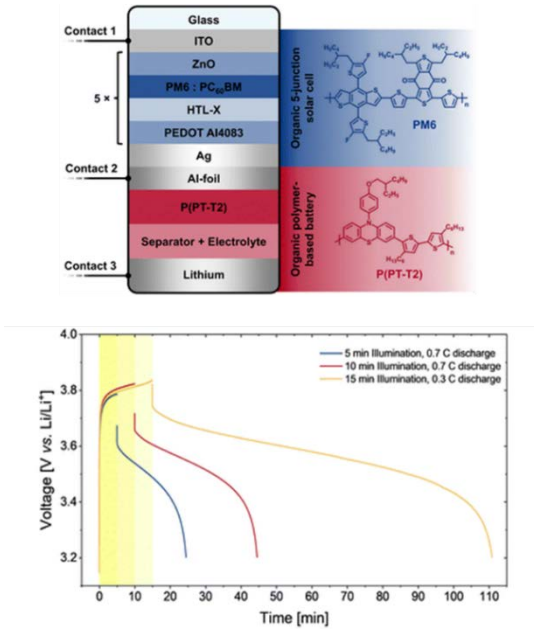

Fig. 4: Schematic layer sequence in the organic photobattery (top) and photocharge and discharge profiles with different illumination times and different discharge rates. Adapted from [6].

The combined device constitutes the first monolithically integrated photo-battery made from organic building blocks capable of reaching competitive voltages sufficiently high for use in small, mobile power devices.

How the carbon additives can influence the performance of polymer-based batteries has been investigated for PVMPT-based systems, typically suffering from polymer leaching over cycling, resulting in the progressive loss of specific capacity over time (PI Fischer, Esser). [7] Here it was demonstrated that depending on the chosen carbon additive and the associated intra- and interparticle porosity, the gravimetric capacity of the polymer battery can be retained and an optimum between stability and capacity retention at high C-rates be found. This clearly demonstrates the underexplored potential of performance optimization which lies in carbon additive mediated electrode structuration.

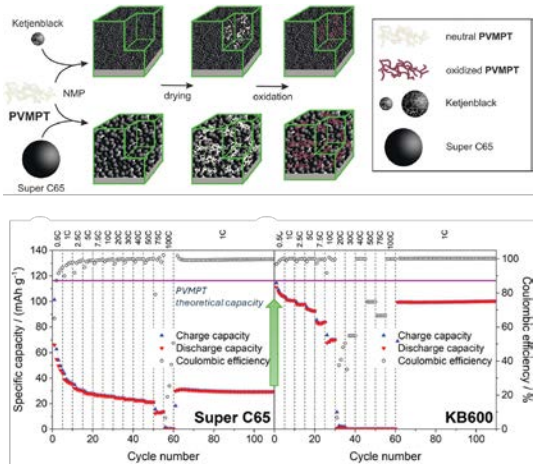

Fig. 5: Schematic diagram of PVMPT-carbon electrodes with Ketjenblack and Super C65 as carbon additive and resulting battery performance. Utilization of Ketjenblack instead of Super C65 results in a massive improvement in terms of the accessible specific capacity. Reproduced from [7]

Outlook

Development of flexible PV units with higher voltages, matching strategies as well as development and integration of post-lithium-ion battery technologies in line with sustainable processing approaches are future research directions which will be followed within the Solstore projects.

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FUTURE FIELD "NEW MATERIALS: SOCIETAL CHALLENGES"

Tiered Approach for Prospective Assessment of Benefits and Challenges (TAPAS) / Sustainability Systems Assessment of the livMatS materials systems for enabling sustainability transitions towards a resource-efficient and resilient infrastructure

Martin Möller[1,2], Rainer Grießhammer[1,3], Harishankar Thekkepat[1]

[1] Cluster of Excellence *liv*MatS @ FIT Freiburg Center for Interactive Materials and Bioinspired Technologies, University of Freiburg, Germany; [2] Öko-Institut e.V. – Institute for Applied Ecology, Freiburg; [3] Faculty of Environment and Natural Resources of the University of Freiburg

Project funding: German Research Foundation (DFG) – Cluster of Excellence "*liv*MatS"

The ultimate goal of the TAPAS project from Research Area D of *liv*MatS was the design of a new, tiered methodological framework (TAPAS) for a prospective assessment of the sustainability aspects of novel technologies and materials systems. TAPAS aims to detect associated benefits and challenges. Hence, the approach serves both as an "early warning system" for less sustainable options and as an "early encouraging system" for favorable paths of innovation. Within this context, TAPAS operationalizes relevant normative frameworks for the sustainability assessment, with particular focus on the 2030 Agenda [1] and the concept of Planetary Boundaries [2]. Furthermore, the project provided important groundwork for the methodological interface between biomimetics and sustainability research by attributing biological concepts to the three sustainability strategies of efficiency, consistency and sufficiency [3].

With the completion of the TAPAS project, a field-proven approach for early sustainability assessment of novel technologies and materials systems is now available. Due to its consistent alignment with the 2030 Agenda, TAPAS combines a high degree of commitment with regard to its indicators with the pragmatic approach of self-reflection. By locating the steps of analysis and assessment in the hands of scientists as the actors of the innovation process, it is not only possible to provide the best possible database; further advantages also arise in terms of "capacity building", i.e. strengthening the methodological knowledge and skills for a sustainability assessment among the users [4].

After successfully defending his PhD thesis in the TAPAS project on February 8, 2023, Martin Möller is now involved in the *liv*MatS cluster as a Responsible Investigator. Since December 2023, he has been supervising the promotion of Harishankar Thekkepat in a newly launched sustainability research project in Area D of *liv*MatS.

This project aims at a further methodological development of the TAPAS framework, which pays special attention to sustainability assessment from a systems perspective, allowing *liv*MatS materials systems and their potential applications to be evaluated in terms of their ability to support sustainability transition processes in key industrial sectors. The evolved methodological framework will be inspired by lessons learned from biological evolution and fitness. In this respect, findings from the TAPAS project will be taken up and further developed for the assessment and strategic optimization of *liv*MatS demonstrators. In particular, this relates to efficiency, consistency and sufficiency, and will provide practical design principles for *liv*MatS materials systems in this respect.

As part of the first work package of the new project, the methodology development started with a gap/needs analysis focusing on technologies and systems required for sustainability transition processes in key industrial sectors towards a resource-efficient and resilient infrastructure. Based on this groundwork, existing assessment systems will be reviewed and a first outline of the new assessment framework will be created.

To test its practicability, the newly developed methodological framework will be applied in up to three case studies covering existing *liv*MatS materials systems at demonstrator level. Based on the results of the analysis, strategic potentials for the optimization of the investigated demonstrators will be proposed and the findings will be condensed into priority future innovation activities for the *liv*MatS Cluster.

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Ethical criteria for life-like materials systems: Interdisciplinary and multimethod approaches

Philipp Höfele[1], Julius Fenn[2], Oliver Müller[3,4], Lore Hühn[3,4], Andrea Kiesel[2,4]

[1]Department of Philosophy, Martin Luther University Halle-Wittenberg; [2]Department of Psychology, University of Freiburg; [3]Department of Philosophy, University of Freiburg; [4]Cluster of Excellence *liv*MatS @ FIT – Freiburg Center for Interactive Materials and Bioinspired Technologies

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Nature-imitating technologies, such as those being developed in *liv*MatS, are currently intensively discussed across numerous natural and technical sciences. They are often considered to be of central importance for technological development in the 21st century [1]. This is because they suggest solutions to sustainability problems in the context of the Anthropocene. At the same time, they pose far-reaching challenges in ethical, legal, and societal terms. Nature-imitating technologies are mostly credited with offering 'better', more ecological and less risky solutions than conventional technologies, which is referred to as the 'biomimetic promise' [2]. From an ethical perspective, however, the question arises as to why and in what respects normative claims such as the 'biomimetic promise' can go hand in hand with such forms of imitation of nature. Natural phenomena and processes can neither be understood as good *per se,* nor can they generally be described as sustainable. Consequently, the mere imitation of natural phenomena and functions is neither 'good' nor sustainable, and in some cases may even result in the exact opposite.

In this respect, the project aims at identifying normative criteria that ensure that the imitation of natural phenomena and functions can be described as 'good' and sustainable. These criteria can help in the ethical evaluation of these emerging technologies during and after the development process and contribute to their sustainability and societal acceptance. This overall goal is to be achieved by means

of three subordinate goals: (a) First, we pursue a theoretical-systematic sub-goal by striving to highlight the historically and socially contingent concepts of nature that underlie the normative orientation towards nature, and investigating what kind of (normative) reference is made to them when we speak of imitation. (b) Then we determine the criteria for the ethical normativity of certain concepts of nature. (c) Finally, we show to what extent the criteria to be determined can only be adequately formulated and implemented in an inter- and transdisciplinary approach.

(a) The first sub-goal intends to show that the nature underlying technical imitation is not a timeless given object, but a historically and culturally conditioned concept that has to be critically reflected upon. At the same time, it is important not to reduce imitation as a relational concept to a reproduction of a natural model without differentiation and innovation, but to understand it as a multi-layered concept that ranges from pure repetition to the reproduction and imitation of a form or of functional principles to more various types of imitation that can be considered as adaptation and 'resonance' [3]. Imitation is generally characterized by a moment of identity as well as difference, whereby one or the other 'pole' can find greater emphasis and normative valence. Furthermore, nature-imitating technologies question the Cartesian dualism that often still dominates debates in the philosophy of technology: the transfer of natural properties and functions into a technical milieu makes them hybrids or 'intermediate beings', similar to the 'biofacts' described by N. Karafyllis [4]. This in turn has repercussions for the concept of nature in the Anthropocene.

(b) From an ethical point of view, the project argues that the concept of imitation, although not in general, can represent a promising ethical principle under certain conditions in view of the pressing environmental-ethical problems that are the focus of the Anthropocene debate. This principle does not fall victim to the naturalistic fallacy articulated by Hume insofar as nature as an object of imitation does not represent a value-neutral space, but, due to its historical and cultural conditionality, as emphasized above, is always accompanied by normative implications. It is necessary to reveal these normative implications underlying the concepts of nature. This can be done, on the one hand, by drawing on historically 'tested' and reflected concepts of nature and, on the other hand, by surveying the normative implications in empirical studies, which is the aim of the following sub-goal. Surveys allow us to explicitly investigate and reflect values and hierarchies accompanying certain contemporary concepts of nature that are apparently taken for granted (e.g. that the natural is perceived as something 'good' *per se*). In this way we can even show that nature-imitating technologies themselves have repercussions on the historically inherited values and hierarchizations. For instance, biomimetic products that prefer the imitation of plant and animal life to intelligent life due to more effective decentralized decision-making processes call traditional value standards into question, insofar as these are to be fathomed relationally in view of the currently determining contexts. The biomimetic transmission process (cf. Fig. 1) thus points in the direction of an ethical relationalism that does not completely reject absolute value standards, but at least relativizes them and thus opens up a space for new, alternative ethical value standards and differentiations that appear to be urgently required in the context of the challenges discussed under the concept of the Anthropocene [5].

(c) Finally, from a methodological point of view, the project aims at interweaving the disciplines of philosophy of nature, philosophy of biology and ethics of technology on the one hand, as well as philosophy, psychology and sustainability research on the other. In view of the challenges discussed under the Anthropocene concept, in particular those of an increasing dissolution of the boundaries between the natural and the human-made, such an interweaving of traditionally disparate disciplines increasingly appears necessary. In particular, nature-imitating technologies pose a challenge in both ontological and ethical terms that cannot be met by any of the aforementioned disciplines alone. If interdisciplinarity and transdisciplinarity are urgently required, especially in the context of the Anthropocene debates [6], this applies equally to evaluation ap-

proaches for emerging nature-imitating technologies. In cooperation with psychological acceptance research, socially dominant images of nature and the normativity associated with them are to be investigated in order to be able to anticipate the possible challenges of the biomitetic transmission process and future nature-human-technology relationships [7].

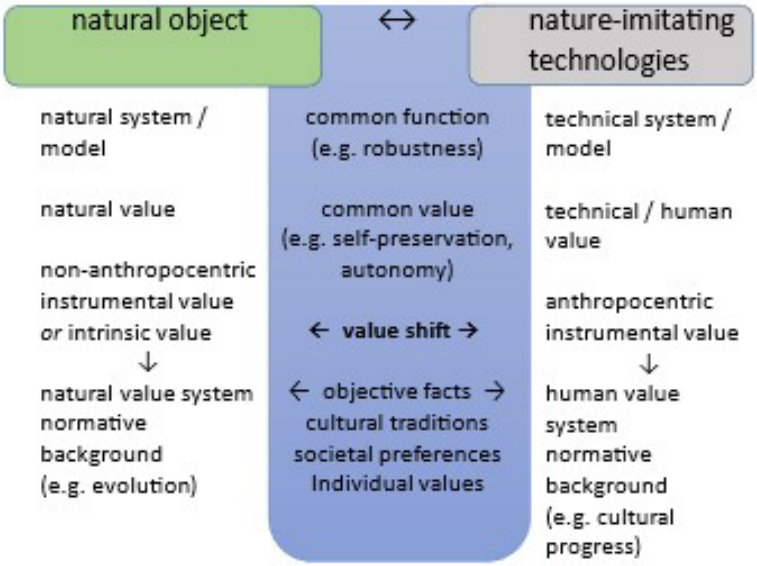

Fig. 1: In the biomimetic transmission process, we identify a natural system or model. Its function is transferred into a technical system or model. Apart from the function that is to be transferred, the natural and technical models are different, as a different technically feasible instantiation of the model is required [8]. The identiefied values, e.g. “self-preservation” or “autonomy”, have a different meaning in the natural and technical milieu. In the one case it is a non-anthropocentric instrumental or intrinsic value, in the other case it is an anthropocentric instrumental value, as the technical device is intended to support humans. (© Cluster of Excellence “Living, Adaptive and Energy-autonomous Materials Systems” (*liv*MatS))

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CORE FACILITY "MODELLING AND SIMULATION OF MATERIALS SYSTEMS"

Expansion of the GPAW XAS simulation to allow simulations with $l_i \geq 0$ using the Delta Kohn-Sham half-core-hole method

Esther Johnsen[1,2], Michael Moseler[1,2,3], Michael Walter[1,2,3]

[1] FIT – Freiburg Center for Interactive Materials and Bioinspired Technologies, University of Freiburg; [2]Cluster of Excellence *liv*MatS @ FIT – Freiburg Center for Interactive Materials and Bioinspired Technologies; [3]Fraunhofer IWM, Freiburg

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Platinum is a well known as an active catalyst, and there are experimental efforts to reduce the size of catalytic sites towards single atoms. Such small structures are difficult to characterize experimentally, and X-ray absorption spectroscopy (XAS) may be used to identify and characterize such structures. The interpretation of the spectra needs a comparison to known standards, which are often not available. Another possibility is to compare to simulated spectra as obtained from state-of-the-art simulations based on electronic structure theory.

The high energy of x-ray photons in XAS excites atomic core-states and is thus element-specific. The thresholds for absorption of these inner states with the main quantum numbers $n = 1,2,3$ are named L -, K-, and M-edges, respectively. The e.g. $M_{2,3}$-edge in iron corresponds to the 3p → 3d transition [1] and the M_2 and M_3 are assigned to spin-orbit-split $p_{1/2}$ and $p_{3/2}$ orbitals, respectively [2]. For platinum, the transitions from the $2p_{1/2}$ and $2p_{3/2}$ orbitals are used, that are known as the L_2- and L_3-edges, respectively [3]. The L_2-edge is found at 13272.6 eV, and the L_3-edge is at 11563.7 eV [4].; resulting in a spin-orbit splitting of 1708.9 eV.

The density functional theory package GPAW co-developed at FIT is capable of efficiently predicting XAS spectra within the Delta Kohn-Sham (Δ-KS) core-hole approach, but so far only for K-edges. We will discuss the expansion of the implementation of the core hole approach for $l \geq 0$, where l is the quantum number of the angular momentum.

The XAS spectra are simulated by calculating the absorption cross-section, $\sigma(\omega)$, which can be obtained from Fermi's golden rule and is proportional to the unit less oscillator strength [5].

$$\left(f_{fi}\right)_\alpha = \frac{2m_e}{\hbar^2 e^2} E_{fi} \left|\langle\psi_f|\left(\hat{D}\right)_\alpha|\psi_i\rangle\right|^2, \quad (1)$$

where m_e is the electron mass, $\alpha = x, y, z$, e is unit charge, ε_0 is the dielectric constant, $\hbar$ denotes the reduced Planck constant, c is the speed of light, ω is the angler frequency, ψ_f is an excited state and ψ_i is the initial (ground) state and $\hat{D}$ denotes the dipole operator, which dictates the behavior of the light matter interaction within the dipole approximation. $E_{fi} = E_f - E_i$ is the difference between the energy of the ground state E_i and the energy of the excited state E_f.

In the core-hole method, we do a ground state calculation with either a half or full core hole in the initial state, ψ_i, and then calculate the dipole matrix element for the unoccupied orbitals (approximating exited states) in the same field. The absolute energy scale is found later using the Δ-KS method. The Δ-KS absolute energy is found by calculating the energy difference between the ground state system and the first excitation that has to be corrected to match experiment [6].

The dipole operator $\hat{D}$ contains the position vector r which can be expressed in terms of x, y and z. The dipole matrix element then becomes the vector

$$D_{fi} = e\langle\psi_f|r|\psi_i\rangle = e\begin{bmatrix}\langle\psi_f|x|\psi_i\rangle\\ \langle\psi_f|y|\psi_i\rangle\\ \langle\psi_f|z|\psi_i\rangle\end{bmatrix}. \quad (2)$$

The initial state is a core-hole state with defined angular momentum l_i and projection m_i. The corresponding wave function, ψ_i, can therefore be separated into a radial wavefunc-

tion, $R(r)$, which is only dependent on the radius and the quantum numbers n and l, and an angular part $Y(\hat{r})$ that only depends on direction $\hat{r}$ and the quantum numbers l and m_l

$$\psi(r) = \sum_l \sum_m R_l(r) Y_{l,m}(\hat{r}). \quad (3)$$

Here $Y(\hat{r})$ is known as the spherical harmonics. The final delocalized state may have contributions from different local atomic angular momenta on different atoms and is expressed in the projector augmented wave method as

$$\psi_f = \tilde{\psi}_f + \sum_a \sum_q P_{fq}^a \left(\phi_q^a - \tilde{\phi}_q^a\right) \quad (4)$$

where $\tilde{\psi}_f$ is the smooth part of the wave function. The ϕ_q and $\tilde{\phi}_q$ are function local to the atom a and their difference is nonzero only within the augmentation sphere. The P_{fq}^a are coefficients, and we note that q is a combined coefficient for the quantum numbers n, l, m. However, only local integrals on the atom a containing the core-hole are non-zero in the calculation of the matrix-element. The matrix element will, therefore, only have contributions from these local parts and may be written as

$$D_{fi} = e \sum_q P_{fq}^a D_{fi,q} \quad (5)$$

with

$$D_{fi,q} = \left[\int_0^\infty R_{n_f l_f} R_{l_i} r^3 dr\right] \cdot \sqrt{\frac{4\pi}{3}} \begin{bmatrix} G_{l_f,l_i,1,m_f,m_i,1} \\ G_{l_f,l_i,1,m_f,m_i,-1} \\ G_{l_f,l_i,1,m_f,m_i,0} \end{bmatrix} \quad (6)$$

for $q = (n_f, l_f, m_f)$ and Gaunt coefficients $G_{l_1,l_2,l_3,m_1,m_2,m_3}$. The oscillator strength eq. (1) can then be expressed as

$$f_{fi} = \frac{2m_e}{\hbar^2 e^2} E_{fi} \left|\sum_q P_{fq}^a D_{fi,q}\right|^2 . \quad (11)$$

The f_{fi} can be seen as a vector as they have three independent components corresponding to three possible independent directions of light polarization.

Transition	Oscillator strengths		
$2s$	TDDFT	KS (HCH-New)	KS (HCH-Old)
$2s \rightarrow 3p$	0.0062	0.0069	0.0069
$2s \rightarrow 4p$	0.0029	0.0021	0.0021

Tab. 1: Oscillator strengths of the Mg atom for the $2s \rightarrow 3p$ and $2s \rightarrow 4p$ transitions calculated by the TDDFT method, and the old and new Δ-KS (HCH) implementation.

We simulate two systems to test the new Δ-KS half-core-hole methode (HCH) implementation. The first system is a single Mg atom, where we compare the f_{fi} produced by our implementation to the results of a computationally much more expensive time-dependent DFT (TDDFT) simulation. We do the simulations for the 2s and 2p initial states. For the 2s calculation the only symmetry allowed transitions are to a p state. For the 2p core-hole we have the transitions to a s state and a more interesting d state. We also compare the 2s transitions the f_{fi} produced by the old implementation.

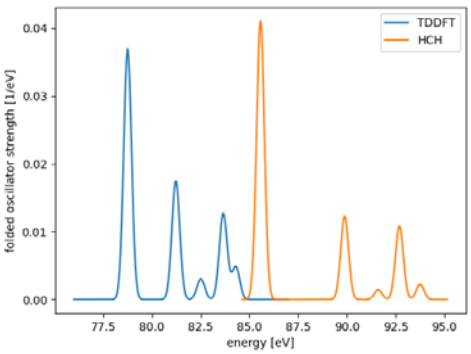

Fig. 1: The simulated XAS spectra of 2s transition for the Mg atom. The spectra produced by the newly implemented Δ-KS HCH method are in orange, and the spectra produced by TDDFT in blue. (© Modelling and Simulation of Materials Systems Group)

The oscillator strengths for the Mg $2s$ transitions, f_{2s}, are found in Tab. 1. Here we present the f_{2s} calculated by TDDFT and the Δ-KS HCH method. The new implementation produces the same oscillator strengths as the previous Δ-KS HCH method, which is a good sanity check of our implementation. Both results

are also in good agreement to the TDDFT calculations giving further confirmation.

Transition	Oscillator strengths	
$2p$	TDDFT	KS (HCH-New)
$2p \rightarrow 4s$	0.0052	0.0035
$2p \rightarrow 3d$	0.0024	0.0019
$2p \rightarrow 3d$	0.0025	0.0022

Tab. 2: Oscillator strength of the Mg atom for the $2p \rightarrow 4s$ and $2p \rightarrow 3d$ transitions calculated by the TDDFT and Δ-KS HCH methods.

Next, we study the oscillator strength for the Mg $2p$ transitions, f_{2p}, found in tab. 2. The evaluation of these within the core-hole approach was not possible before. For the $2p$ transitions there are two nonzero transitions by symmetry, namely $p \rightarrow d$ and $p \rightarrow s$.

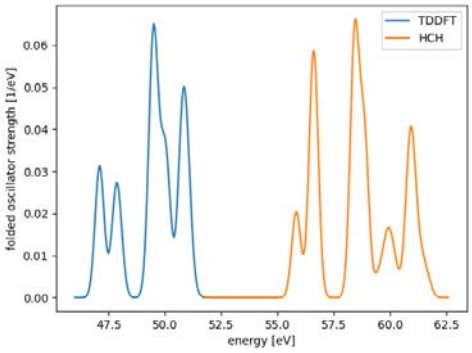

Fig. 2: The simulated XAS spectra of 2p transition for the Mg atom. The spectra produced by the newly implemented Δ-KS HCH method are in orange, and the spectra produced by TDDFT in blue. (© Modelling and Simulation of Materials Systems Group)

Comparing the f_{2p} for the TDDFT and Δ-KS HCH method, we see that the Δ-KS HCH are consistently lower than for the TDDFT calculations. However, the oscillator strengths are still in good agreement with each other, which validates the new implementation.

Figures 1 and 2 compare the XAS spectra produced by the TDDFT and HCH methods for the 2s and 2p transitions for the Mg atom in gas phase, respectively. Both figures show that the absolute energy between the TDDFT and HCH spectra are shifted. The underlying reason for this is poorly understood and requires correction for a direct comparison between simulation to the experiments on the absolute energy scale. The spectra are otherwise in reasonable agreement to each other with small deviations that may result from weaknesses in either method.

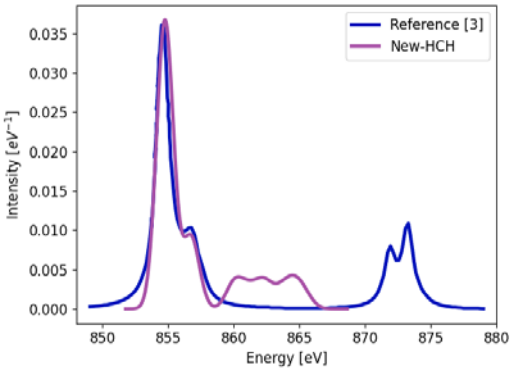

Fig. 3: The simulated XAS spectra of 2p transition for the NiO molecule. The spectra produced by the newly implemented Δ-KS HCH method is in purple, and the reference spectra produced by F.M.F. de Groot [3] are in blue, on a NiO crystal using crystal field multiplet model. The data for the reference spectra was obtained using webplotdigitizer, and the spectra have been scaled so we have the same intensity, as the reference spectra used a.u. for the intensity. (© Modelling and Simulation of Materials Systems Group)

The second system under study is a NiO. Here we compare our simulated spectra for the $2p$ transitions within a single NiO molecule to the literature, specifically to the simulated spectrum produced by de Groot et al. [3] . Fig. 3 shows this comparison. The blue spectrum represents the simulated XAS spectrum for the $2p \rightarrow 3d$ transitions using theΔ-KS HCH method in gas phase, while the purple spectrum is a reference spectrum calculated by F.M.F. de Groot et. al. in a crystalline structure using the crystal field multiplet model [3]. We have scaled the reference spectrum to match the intensity of the Δ-KS HCH simulation. The agreement between the two spectra further validates the correctness of our implementation of the expansion of the XAS simulation.

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Binding Energy and XPS Calculations of Methanethiole Molecules on the Gold Surface (FCC111)

Zohreh Izadi[1,2], Leonhard Mayrhofer[3], Michael Moseler[1,2,3], Michael Walter[1,2,3]

[1]Cluster of Excellence livMatS, University of Freiburg, [2]Institute of Physics, University of Freiburg, Hermann-Herder-Str. 3, 79104 Freiburg, Germany,[3]Fraunhofer IWM, MikroTribologie Centrum µTC, Wöhlerstrasse 11, D-79108 Freiburg, Germany.

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Triboelectricity, a phenomenon rooted in the electrostatic charging of materials upon mechanical contact, has fascinated scientists and engineers for centuries. In a joint effort between the experimental groups Balzer/Esser/Fischer and theory by Moseler/Walter we investigate redox-active molecules anchored on gold surfaces on their triboelectric effects. The connection to the surface is ensured by thiol-binding that is known to form strongly bound self-assembled monolayer structures. This interaction ensures a stable and well-defined interface, allowing for precise investigation of charge transfer mechanisms. Additionally, gold surfaces are known for their high conductivity and stability, making them an ideal substrate for investigating electronic interactions with organic molecules, offering invaluable insights into triboelectric phenomena at the molecular level.

In this study, we used the concept of binding energy and X-ray Photoelectron Spectroscopy (XPS) calculations for our investigation.

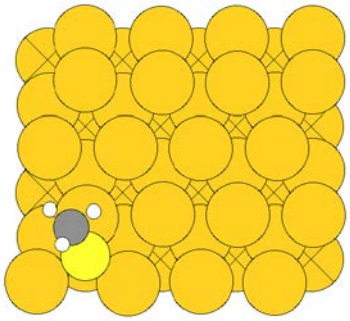

Fig. 1: Hollow configurations of SCH3 molecule on Gold surface (FCC111) (© Modelling and Simulation of Materials Systems Group)

We employed GPAW [1], a density-functional theory (DFT) Python code based on the projector-augmented wave (PAW) method and the atomic simulation environment (ASE) for the calculations. The Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional [2] was utilized, along with van der Waals (vdW) corrections [3] for density functional theory (DFT) calculations. A convergence threshold of fmax=0.02 was applied to ensure accurate results. In our X-ray Photoelectron Spectroscopy (XPS) analysis, we implemented the off-

set-corrected Δ-Kohn-Sham scheme, as introduced by Walter, Moseler, and Pastewka [4] that allows to predict XPS spectra on the absolute energy scale.

We considered different reactions involving the smallest thiol, methanethiol as example case. We bind methanethiol radicals (SCH_3) to the gold surface, emphasizing the analysis of binding energies to find out the favorable molecule-surface interactions. Among the explored scenarios, which included the formation of dimer (H_3CSSCH_3), adsorption of H_2 produced in the reaction, and direct bonding with the surface, the most probable scenario is that the SCH_3 radical directly binds with the gold sublayer, yielding a large binding energy of 2.41 eV.

In pursuit of enhanced calculation accuracy, we considered different binding sites for the SCH_3 molecule and our calculation indicated that the most stable adsorption configuration on the FCC111 gold is the hollow site (Fig. 1).

We are now interested, whether it is possible to observe the binding in XPS spectroscopy. We present XPS analyses of S(2p) spectra in Fig. 2, comparing simulated results for bound SCH_3 thiol on the FCC111 gold sublayer (Fig. 2) with experimental spectra of C16-bound thiol by Castner et al. [5]. Significantly, our simulation shows excellent agreement to the experimental data, affirming the accuracy of our computational approach.

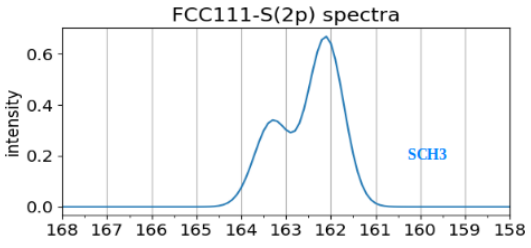

Fig. 2: XPS Analysis of S(2p) Spectra for bound SCH3 Thiol on the FCC111 Gold surface (Simulation), compare to the XPS S(2p) Spectra for C16 bound Thiol in experiment, Fig. 1 in Ref. [5]. (© Modelling and Simulation of Materials Systems Group)

Castner et al. also reported spectra of partly bound thiols that show markedly distinct spectra. Extending our investigation to include both bound and unbound thiol on the FCC111 gold surface, our calculations reveal that the unbound thiol corresponds to the Dimer (H_3CSSCH_3 molecule), while the bound thiol is the SCH_3 radical (Fig. 3).

We compared these results with experimental XPS spectra of PMMPS-bound and unbound thiol, as shown in (Fig. 3.b) by Castner et al [5]. As evident in the spectra, the initial peak corresponds to the bound thiol, positioned at a lower energy range of around 162 eV, while the peaks for the unbound thiol are approximately 2 eV higher.

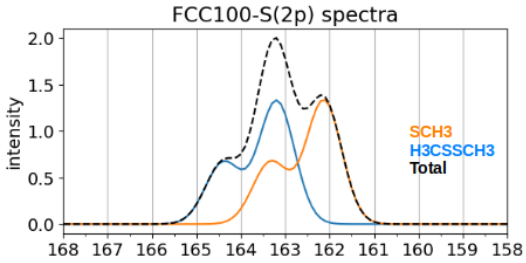

Fig. 3: XPS Analysis of S(2p) Spectra for bound SCH3 and unbound H3CSSCH3 Molecules on the FCC100 Gold surface (Simulation), compare to the XPS S(2p) spectra for PMMPS bound and unbound Thiol in experiment, Fig. 1 in Ref. [5]. (© Modelling and Simulation of Materials Systems Group)

In conclusion, this strong agreement between our simulation and experimental measurements indicates the reliability of our computational methodology and deepens our understanding of molecular interactions on the gold surface.

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Predicting Carbene's Stability from First Principles

Eleonora Galli[1], Dr. Dennis Rusitov[1,2], Prof. Dr. Jürgen Rühe[1,2], PD Dr. Michael Walter[1]

[1]Cluster of Excellence *liv*MatS @ FIT – Freiburg Center for Interactive Materials and Bioinspired Technologies; [2]Department of Microsystems Engineering, University of Freiburg

The objective of this research is to investigate the activation energy of carbenes, highly reactive species composed of a divalent carbon atom. Carbenes play a crucial role as versatile intermediates in various organic chemistry processes, such as Carbon-Hydrogen insertion [1]. The production and investigation of carbenes with tailored properties often face experimental limitations, causing some possibly valuable options to be overlooked due to time-consuming, complex, or economically expensive processes. The computational approach employed in this project overcomes such limitations by calculating the activation energy of carbenes from first principles: by exploring the impact of various substituents on the carbene's activation energy, we provide a predictive guideline for assessing the influence of other substituents.

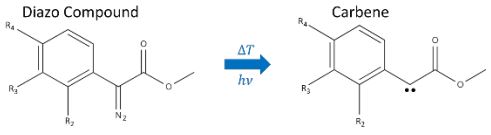

Fig. 11: Carbenes are synthesized from the removal the diazo group from a diazo compound by providing thermal or light energy. (© Modelling and Simulation of Materials Systems Group)

We employ Density Functional Theory (DFT) as implemented in the GPAW package [2] co-devoloped at FIT for ab initio calculations of activation energy. The activation energy of carbenes is defined as the energy required to remove the diazo group from a diazo compound, resulting in the production of a carbene (Figure 1). Experimentally, this energy is provides by thermal sources or light. In other words, the carbenes' activation energy is the binding energy of the diazo group, defined as the difference between the fundamental state energy of the diazo group and the fundamental state energies of the isolated carbene and diazo groups:

$$E_{binding} = E_{diazo} - (E_{carbene} + E_{N2}).$$

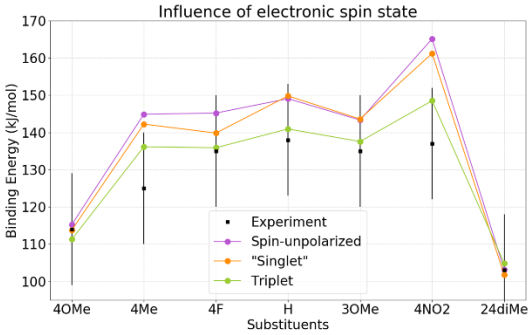

Fig. 2: The comparison of spin-unpolarized and spin-polarized calculations show that the energy minimum is reached when the triplet state is fixed. The calculations with $S_z = 0$, here labeled as "Singlet", are influenced by the triplet state, explaining why very similar results are obtained for the different spin-polarized calculations for some substituents. Particularly remarkable is the agreement of the simulation results with the experimental data. (© Modelling and Simulation of Materials Systems Group)

Carbenes can exist in singlet and triplet states, and their electronic spin state significantly influences their properties, including their reactivity. It is therefore essential for our study to identify the actual spin state with the lowest energy, hence the necessity to conduct spin-polarized calculations. DFT doesn't allow drawing a clear distinction between the singlet and triplet state as only the projection Sz of the spin onto a virtual axis can be fixed, but not the total spin S. As a consequence, spinpolarized calculations with Sz = 0 could converge either to a singlet state or to a triplet state. To identify the spin-state we exploit a property of carbenes: these molecules are characterized by specific binding angles depending on the electronic spin state (~130° for the triplet state and ~100° for the singlet state). The analysis of the

binding angle of carbenes with various substituents shows that the triplet state affects also the spin-polarized calculations with Sz = 0. This suggests that the triplet state carbenes are more energetically stable than the singlet state carbenes. In addition, the triplet state carbenes have lower activation energy for most substituents, as shown in Figure 2. The results are in excellent agreement with the experimental data demonstrating the high reliability of our model.

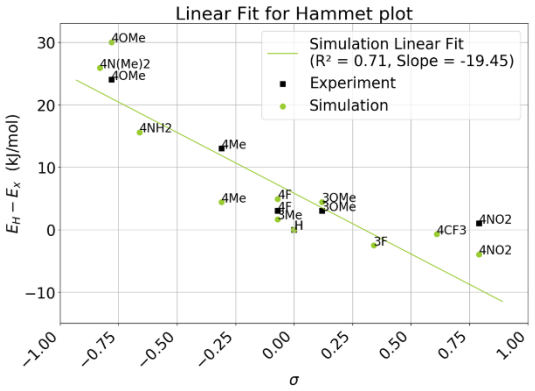

Fig. 3: The calculations of the activation energy of carbenes with various substituents, show that the difference $E_H - E_X$ is linear in the Hammett parameter σ, where σ>0 corresponds to electron-withdrawing effects of the substituent, while σ<0 indicates electron-donating effects. This linear relation can be used to predict the activation energy E_X of carbenes with any substituent X. (© Modelling and Simulation of Materials Systems Group)

Figure 2 also shows that the binding energy of the diazo group depends on the substituents in the aromatic ring. The activation energy of the carbenes could therefore be tuned for specific applications by choosing the appropriate substituent. Hence, we investigate the influence the substituents on the carbene's activation energy. Experimental studies suggested that the activation energy of carbenes could be described by Hammett parameters, a set of empirical constants that quantify the electronic effects of substituents on the reactivity of aromatic compounds [3,4]. Our model indeed shows a linear relationship between difference between activation energy of the carbene without any substituent and that of the carbene with a given substituent X (Figure 3). The Hammett parameters can be used as a rule of thumb to predict the substituent's impact on the activation energy, aiding in selecting the optimal substituent for specific applications.

Further research could involve the investigation of the photon activation of carbenes, and the study of the influence of other functional groups at different positions in the molecule.

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PROJECTS

GROWBOT—TOWARDS A NEW GENERATION OF PLANT-INSPIRED GROWING ARTEFACTS

T. Speck[1,2]

[1]Plant Biomechanics Group Freiburg, Botanic Garden, University of Freiburg; [2]Freiburg Center for Interactive Materials and Bioinspired Technologies (FIT)

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The European project GrowBot - Towards a new generation of plant-inspired growing artefacts formally ended on 30 June 2022. It proposed a disruptive new paradigm of motion in robotics, inspired by the movement-by-growth capabilities of climbing plants, and even after the formal end of the EU project, there is a close collaboration between the project partners, as evidenced by an increasing number of joint publications in 2023 and beyond [e.g. 1-5].

Fig. 1: GrowBot - Towards a new generation of plant-inspired growing artefacts. Figure from www.growbot.eu.

After the end of GrowBot, there is a better understanding of the potential of plants as models for robotics and soft machines, but there are still many important and interesting aspects that remain unexplored. One of the reasons why plants are still not considered as concept generators for soft machines and soft robots is (mostly) their sessile nature, which leads to the assumption that they do not move. In fact, they move quite a lot, but on a different time scale. To move from one point to another, plants have to grow and continuously adapt their bodies to the external environment. This continuous growth is particularly evident in climbing plants.

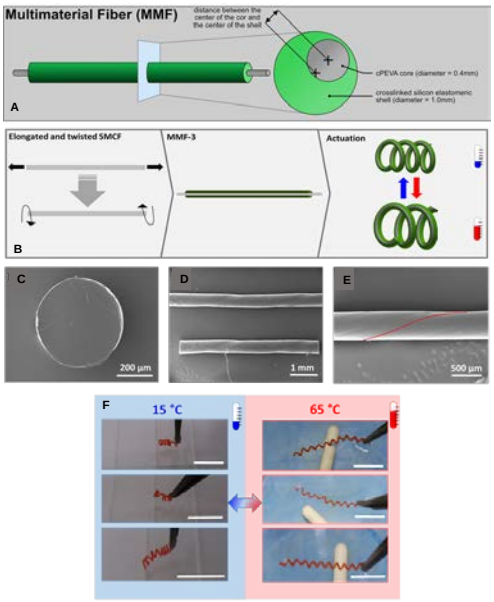

Fig. 2: A) Structural setup of a multimaterial fiber. B) Multimaterials fiber of type 3 (MMF-3) are prepared from deformed shape memory core fibers (deformation by stretching and twisting). They show reversible change in number of coil, coil diameter and tendril length on cyclic heating and cooling. C)-E) SEM images of a cross section of a twisted shape-memory core fiber of the core-shell multimaterial fibers (MMFs). The core fiber is made of crosslinked poly(ethylene-*co*-vinyl acetate (cPEVA) (scale bar: 200 µm). Surface of the core fiber without (scale bar: 1 mm) and with a red guide line highlighting the spiral surface structure in the twisted fiber (scale bar: 500 µm). F) Image series showing reversible opening and closing of three different MMF tendrils on heating and cooling, during the 3rd heating–cooling cycle (scale bar 2 cm). Figure adapted from [1].

Based on detailed quantitative analyses of the biomechanics and underlying structures of plant, and in particular liana, movement [2-4], the goal of GrowBot was to develop low mass and volume robots capable of anchoring themselves, negotiating voids and, more generally, climbing where current climbing robots based on wheels, legs or rails get stuck or fall [6]. A specific aim in GrowBot was to develop liana-inspired actuators and sensors [1,5] and to translate the ability to grow through additive manufacturing processes inside the robot, which creates its body by depositing new materials with multi-functional properties based on perceived external stimuli (without a pre-

defined design). Perception and behaviour are inspired by the adaptive strategies that allow climbing plants to explore their environment [5]. GrowBot is based on a strongly interdisciplinary approach and can open the way for a new technological paradigm around the concept of growing robots, fostering a European innovation ecosystem for several high-tech sectors [6].

The Plant Biomechanics Group Freiburg contributes to this task based on its long experience in eco-biomechanics and stem structure of climbing plants, on the different attachment systems existing in climbing plants and on its expertise in the development of bio-inspired materials systems. In recent years, we have focused on the function of tendrils and intertwining liana stems as models for novel soft machines and soft robots. In collaboration with colleagues from the Italian Institute of Technology and the Helmholtz Centre Herion, two types of bioinspired soft machines have been developed and realised [1,5].

In the GrowBot project in Freiburg, basic research has focused on the sophisticated anchoring system(s) of various *Passiflora* species. Many species have developed tendrils that are able to "grasp" thin supports (so-called contact coiling), while other species have developed adhesive pads at the tips of the tendrils that allow them to adhere to a wide range of different substrates [2-4]. In addition to the performance of individual tendrils or even individual adhesive pads, the interaction of multiple tendrils is a future target of investigation. Using *Passiflora discophora* as an example, it has been shown that the adhesive pads of multiple tendrils act together under load (rather than breaking off one by one). This allows the plant to withstand relatively large external forces before being torn from its substrate [2]. All *Passiflora* tendrils have in common that – as they mature – they coil around their longitudinal axis (free coilng), thereby shortening themselves and tying the plant stem firmly to its support structure [3,4]. Using a self-developed experimental setup, we were able to measure the forces during this coiling process in vivo for the first time, and even relate them to the hydration status of the plant [3]. We also published a form-structure-function model of the driving forces for free coiling and compared the coiled structures with conventional engineering spring blades [4]. These studies provided the scientific basis for biomimetic polymer-based artificial tendrils. The artificial tendrils developed and produced in collaboration with the Helmholtz Centre Herion are core-shell multimaterial fibres (MMFs) consisting of a shape-memory core fibre made of crosslinked poly(ethylene-co-vinyl acetate) (cPEVA) and an elastic silicone shell. They represent small soft machines that can be used as linear motors in more complex soft climbing robots (see Figure 2) [1,6].

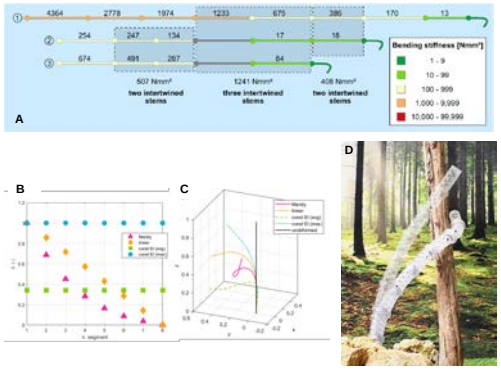

Fig. 3: A) Values of flexural rigidity obtained by 3-point bending tests on searcher stems of *Mandevilla* cf. *splendens*. Each of the three schematic stems represents a stem in a braided structure composed of three. The main stem is denoted by n.1. The dashed rectangles enclose regions of braided stems, with the flexural rigidity resulting from the braiding reported below. B) Distributions of flexural rigidity in the four continuum "Mandybots" considered to simulate the mechanical response under C). The simulations and experiments show that only with a flexural rigidity distribution as in the searcher twigs of of *Mandevilla* cf. *splendens* the MandyBot (with a helically deployed tendon with ϕ = 22.5°) is able to twin around a supporting structure. D) Twining of a MandyBot robot arm. Figures A-C adapted from [5], figure D courtesy of Giovanna Naselli (IIT).

In a collaborative project with the Italian Institute of Technology (IIT), we investigated how soft continuum arms can benefit from mimicking the distribution of flexural rigidity of searcher stems found in stems of climbing plants to achieve 'intelligent' behaviour while minimising sensing, actuation and control effort [5]. Based on and inspired by studies on the distribution of flexural stiffness of single and intertwined searcher stems of *Mandevilla* cf. *splendens*, a modelling approach was developed to tune both the structural design and

the tactile sensor design of a soft continuum arm. The resulting soft continuum arm, named MandyBot, can detect suitable supports along its length and wrap around them using a single sensor and actuator. It was shown that such behaviour could not be achieved with a soft continuum arm with uniform structural stiffness and a standard tactile sensor design, but with the MandyBot arm having a bending stiffness distribution as found in the searcher branches of *Mandevilla* cf. *splendens* (see Figure 3) [5].

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DELIVER

Carl-Zeiss-Stiftung supports research project on wood-based materials at the University of Freiburg

Tom Masselter[1,2], Clemens Kreutz[3], Thomas Speck[1,2], Wilfried Weber[4]

[1]Plant Biomechanics Group (PBG) Freiburg @ Botanic Garden of the University of Freiburg, [2]Freiburg Center for Interactive Materials and Bioinspired Technologies (FIT), [3]Institute of Medical Biometry and Statistics (IMBI), University Medical Center Freiburg, [4]INM – Leibniz Institute for New Materials and Saarland University, Department of Materials Science and Engineering

The DELIVER project is creating sustainable biocomposites based on sawdust glued together by proteins produced by programmable microorganisms in the material.

In the DELIVER project, scientists seek to develop sustainable wood-based materials whose properties can be precisely controlled. Photo: Benedikt Falkenstein

The Carl Zeiss Foundation is funding the "DELIVER - Data-driven Engineering of Sustainable Living Materials" project at the University of Freiburg in its "CZS Wildcard" program. In the project, scientists from the Freiburg Clusters of Excellence CIBSS and *liv*MatS will develop sustainable wood-based materials whose properties can be precisely controlled. The materials are based on microorganisms that produce proteins and can use them to combine wood waste (sawdust, wood chips) into biocomposites. The researchers will direct this process using optogenetic methods to obtain materials with controllable properties that will be characterized using various methods. The project receives 750,000 euros over two years. It is coordinated by **Wilfried Weber**, who recently joined the INM – Leibniz Institute for New Materials in Saarbrücken.

Approach based on the intersection between materials science, synthetic biology and machine learning

DELIVER is inspired by the ability of living organisms to produce materials with specific properties adapted to external conditions. The scientists will make use of this ability. The goal of the project is to design wood-based multimaterial systems whose mechanical properties and appearance can be specifically targeted. “We are treading a completely new path with our approach, as it starts at the intersection between materials science, synthetic biology and machine learning,” says **Thomas Speck**, a biologist in the Cluster of Excellence Living, Adaptive and Energy-autonomous Materials Systems (*liv*MatS). Together with **Tom Masselter**, he is responsible for characterizing the physical and mechanical properties of the multimaterial systems in the DELIVER research team.

Controllable material properties through optogenetics

The researchers will use optogenetic methods to modulate the material properties. These methods can be used to influence the information processing of cells, which controls how external stimuli are interpreted and which genetic programs are activated in the cells. “We use light of specific wavelengths with which we locally irradiate the microorganisms as a stimulus,” **Wilfried Weber** explains. “In this way, we activate genetic switches that direct the production of specific proteins.” This makes it possible to direct which proteins are released by the bacteria and yeasts, which are used to bind sawdust, wood chips or other, agricultural waste. The resulting biocomposites are then baked to kill the bacteria.

Database with custom fit materials

In the future, adjusting various parameters during the production process will enable the achievement of a diverse range of material properties. Consequently, this project aims to establish a knowledge base for recording and predicting material properties, such as those derived from genetic programming. To predict and optimize new material properties, we will employ various machine learning techniques, a project part led in the research team by **Clemens Kreutz**. Robots will automatically synthesize the different material variants and perform mechanical tests. Based on the database, it will be possible in the future to specifically generate and optimize materials with desired properties, for example for furniture construction.

IPROM—Interactive and programmable materials

Jürgen Rühe[1,2], Bastian E. Rapp[1,3]

[1]Cluster of Excellence livMatS @ FIT – Freiburg Center for Interactive Materials and Bioinspired Technologies, University of Freiburg, Georges-Köhler-Allee 105, D-79110 Freiburg, Germany; [2]Laboratory for Chemistry and Physics of Interfaces, Department of Microsystems Engineering (IMTEK), University of Freiburg; [3]Laboratory of Process Technology (Neptun Lab), Department of Microsystems Engineering

Project Funding: Carl Zeiss Foundation

www.fit.uni-freiburg.de/iprom

One of the core principles in the design of technical objects is the static nature of the materials: They have more or less unchangeable properties. In nature, on the other hand, the (bio-)materials used by living systems are geared towards enabling the best possible adaptation to the respective environmental conditions in order to be best react to changes in the surrounding. The aim of the Research Cluster "Interactive and Programmable Materials (IPROM)" funded by the Carl Zeiss Foundation is the development of innovative technical materials that respond to changing environmental conditions with a response, which is preprogrammed into the material and thus triggers a material adaptation to changes in the surrounding and the load conditions. In order to do so, they have to be able to change their internal structure and/or their external shape as a consequence of an external stimulus, e.g. by adapting the adhesion, wettability or mechanical properties of the materials. This concept opens up new opportunities for the production of complex objects in many areas such as optics, medical technology or architecture.

"The IPROM cluster will bring forth a paradigm shift in materials research from static to dynamic materials. The novel materials generated will dynamically adapt their properties to the constantly changing conditions of their environment in a previously programmed manner."

Fig. 1: IPROM – Interactive and Programmable Materials (www.fit.uni-freiburg.de/iprom)

IPROM projects include the following topics:

TP 1: Bio-inspired programmable material systems (PI: Thomas Speck)

TP 2: Multiparameter / Multimaterial 4D Printing (PI: Bastian E. Rapp)

TP 3: Light-responsive surfaces (PIs: Jürgen Rühe & Bastian E. Rapp)

TP 4: Nonlinear micromechanics of programmable materials (PIs: Christoph Eberl & Lars Pastewka)

TP 5: Sustainable materials for 4D printing (PI: Dorothea Helmer)

TP 6: Programmable Tribology (PIs: Jürgen Rühe & Lars Pastewka)

TP 7: Biocompatible, programmable materials for soft micro-robots (PI: Karen Lienkamp)

TP 8: Bioelectroactive Interfaces for dynamic interaction with biology (PI: Maria Asplund)

TP 9: Autonomous and reconfigurable metamaterials and soft robots (PI: Andreas Walther)

TP 10: Digitized dynamic illumination (PI: Hans Zappe)

LIVING, ADAPTIVE AND ENERGY-AUTONOMOUS MATERIALS SYSTEMS (*liv*MATS)

Prof. Dr. Jürgen Rühe[1,2,3], Prof. Dr. Anna Fischer[1,2,4], Prof. Dr. Thomas Speck[1,2,5]

[1]Cluster of Excellence livMatS @ FIT – Freiburg Center for Interactive Materials and Bioinspired Technologies, University of Freiburg, Georges-Köhler-Allee 105, D-79110 Freiburg, Germany; [2]Freiburg Materials Research Center (FMF), University of Freiburg, Stefan-Meier-Str. 21, 79104 Freiburg, Germany; [3]Laboratory for Chemistry and Physics of Interfaces, Department of Microsystems Engineering (IMTEK), University of Freiburg, Georges-Koehler-Allee 103, D-79110, Freiburg, Germany; [4]Inorganic Functional Materials and Nanomaterials, Institute for Inorganic and Analytical Chemistry, University of Freiburg, Albertstr. 21, 79104 Freiburg, Germany; [5]Plant Biomechanics Group (PBG) and Botany: Functional Morphology and Biomimetics @ Botanic Garden of the University of Freiburg

Project funding: Funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) under Germany's Excellence Strategy – EXC-2193/1 – 390951807

The Cluster of Excellence "Living, Adaptive, and Energy-autonomous Materials Systems" (*liv*MatS) develops bioinspired materials systems that adapt autonomously to various environments and harvest clean energy from their surroundings. The aim of these purely technical – yet in a behavioral sense – quasi-living materials systems is to address human needs for groundbreaking environmental and energy technologies. The societal relevance of autonomous systems and their sustainability thus plays a crucial role in their development within the framework of *liv*MatS. The Cluster receives fund-ing from the German Research Foundation (DFG) under Germany's Excellency Strategy – EXC-2193/1 39051807 since January 2019.

Goal of the Cluster is that bioinspired mate-rials, efficient energy materials systems (harvesting, conversion, and storage), and interactive, self-repairing materials with different and often even contradictory properties and functional conditions all meet to form a quasi-living materials system. *liv*MatS materials systems have four core properties which accordingly align with its four research areas: A – Energy Autonomy, B – Adaptivity, C – Longevity, and D – Sustainability (cf. Fig. 1). Research from

all four areas feeds into demonstrator projects [1].

Fig. 1: Interplay of the closely interconnected Research Areas in *liv*MatS (A – Energy Autonomy, B – Adaptivity, C – Longevity, D – Sustainability and Societal Implications). © *liv*MatS / Daniel Hellweg.

Research area A – Energy Autonomy studies novel methods of energy harvesting and/or energy storage within a single highly integrated system, i.e. aims to develop materials systems with embedded energy and energy management. Light, temperature differences, and vibrations are used as potential sources of energy. Once harvested, the energy is either consumed directly or stored for later use. Another important factor is the transformation of energy, making it available in mechanical, chemical, or thermal form or as light energy for adaptive processes within a materials system.

Research area B – Adaptivity develops new concepts for adaptive materials systems with complex energy landscapes that recognize and can react to sensory input from their environment. The recognition of the sensory input and the reaction to it are not performed by a sensor/computer combination but directly by the material or the materials system itself, using energy harvested from the environment. The goal of the research in area B is to develop a materials system with a “memory” that can adapt to its environment and improve itself.

Research area C – Longevity develops strategies that focus on the longevity and “self-control” of complex materials systems, drawing inspiration from living nature, particularly plant life. In other terms, it aims to develop materials systems with embedded intelligence. Mechanisms for self-repair, the shedding and replacement of damaged parts, or also a training-based strengthening of system parts under special stress help to prevent minor damages from leading to a loss of functioning of the entire system.

Research area D – Sustainability considers the societal dimension of autonomous, quasi-living materials systems and their sustainability. A societal discourse on disruptive technologies, such as autonomous driving or expert systems, is often conducted only after developing and introducing these technologies. In *liv*MatS, this discourse is initiated as the technologies are being developed. The goal is to strengthen the development of the materials systems by means of concurrent sustainability analyses. Moreover, we want to actively explore their societal dimension by engaging in critical philosophical reflection and conducting psychological studies.

There are myriad potential applications for the materials systems developed in *liv*MatS. Examples are “soft” machines that can recognize and grasp objects by feeling them, without the help of a computer, or can autonomously walk controlled by pneumatic logic gates. Materials systems that can adapt to temperatures, lighting conditions, or pressure would also open up a wide range of application areas, such as protective clothing (like helmets and back protectors) or prostheses that can adjust themselves to fit the wearer automatically, autonomously and without needing external energy supply – for instance through the use of body heat. Other ideas include packaging materials that grow stronger automatically when placed under stress, and building envelopes that level out temperature differences, for example to prevent overheating.

*liv*MatS is based at the Freiburg Center for Interactive Materials and Bioinspired Technologies (FIT) and unites researchers from the Faculty of Engineering, the Faculty of Chemistry and Pharmacy, the Faculty of Biology, the Faculty of Mathematics and Physics, the Faculty of Economics and Behavioral Sciences, and the Faculty of Humanities. Our institutional composition reinforces the university’s strategic alliance with Freiburg’s Fraunhofer

Institutes, with the Fraunhofer Institute for Solar Energy Systems (ISE) and the Fraunhofer Institute for Mechanics of Materials (IWM) as partner institutions within the Cluster, and is complemented by the Institute for Applied Ecology (Öko-Institut e.V.).

*liv*MatS uses the ideas factory (IDEASfactory@FIT) to implement new forms of scientific exchange and interdisciplinary cooperation. Three shared laboratories, one for the Research Areas A, B and C each, foster close collaboration between researchers within and across research areas. Shared Lab A provides equipment for the synthesis, modification, and processing (2D and 3D) of energy materials as well as advanced photochemical, electrochemical and microscopic characterization. Shared Lab B focuses on microscopy, spectroscopy and rheology, with additional equipment for wet lab chemistry and sample preparation. It also provides an X-ray photoelectron spectroscopy system (XPS) for surface analysis with microscopic resolution and depth profiling. Shared Lab C provides additional options for microscopy and imaging but has its main focus on materials testing from macro- to microscale, 3D & 4D printing, and sample preparation. The core equipment includes a top-of-the-line direct laser writing /2photon lithography setup, a MicroCT system with an integrated mechanical testing device for the quantitative structural analysis of biological structures and biomimetic materials systems, and an electrospinning setup for the processing of polymer and polymer-composite materials into porous felts, among others.

Since 2019, the Cluster has developed and set up three different types of projects to provide flexible formats for the implementation of its research agenda. Doing so has allowed us to strike a balance between long-term projects (36 months) and complementary booster and impulse projects (six to eight and three months respectively). The first cohort of PhD researchers from the Cluster's long term projects started in 2019. In 2023, they completed their theses and graduated. Accordingly in 2023, 16 new long-term projects started, welcoming a new cohort of 24 PhD researchers and 5 postdocs to work on collaborative topics across all research areas and the demonstrator area. In addition, 21 booster projects were completed in 2023, adding to the Cluster's scientific positioning and output. The final generation of long-term projects for the first funding period were selected in summer 2023, with a total of 13 long-term projects that have started since late 2023.

Over the past 5 years, *liv*MatS has been able to recruit excellent researchers for its projects. In December 2023, over 200 researchers at all levels (from doctoral researchers to experienced principal investigators) have worked or are working in projects directly funded by the Cluster or associated to it. In 2023, *liv*MatS filled its two cluster professorships with high-profile candidates: one for the tenure track professorship "Soft Machines" at the Faculty of Engineering and the other for a W3 professorship "Active Soft Matter" at the Faculty of Chemistry and Pharmacy. In addition, the Cluster was able to hire a fifth Junior Research Group Leader on the topic of "Bioinspired Materials Concepts".

The achievements of *liv*MatS scientists are reflected in awards their work has received in 2023. Chemist and PI Dr. Charalampos Pappas has been awarded an ERC Starting Grant for his research on self-assembling materials. The European Research Council also honored chemist and PI Prof. Dr. Laura Hartmann with an ERC Consolidator Grant for her research into recreating the glycocalyx, a thick layer of sugars that coat our cells. Young scientists from *liv*MatS were also honored in 2023. Dr. Max Mylo received a Camillo Schneider Award from the German Dendrological Society for his dissertation in which he investigated how plants prevent, mitigate or control damage. Dr. Lisa Reuter was honored with the Erasmus Prize for the Liberal Arts and Sciences of the University of Freiburg for her dissertation, in which she investigated the possibilities and limits of "Cognitive Affective Maps" (CAMs).

With fewer pandemic-related constraints in 2023, *liv*MatS has continued its efforts to promote internal and external scientific exchange and interaction with the public, with a strong focus on re-establishing onsite formats. From March 21st – 24th, 2023, *liv*MatS hosted the "1st

International Conference and Scientific Exhibition on Living Materials Systems" as an onsite event in Freiburg. More than 180 researchers discussed intelligent materials systems across disciplinary boundaries. The program included plenary and invited talks from leading researchers in their respective fields, a total of five parallel sessions on different aspects of living materials systems, as well as daily poster sessions. Special issues with contributions from the conference are currently being prepared. All members of the *liv*MatS community came together for the Cluster's fifth scientific retreat from November 30th – December 1st, 2023. During the onsite event in Breisach, the current status, challenges, interfaces and goals of collaborative research in *liv*MatS were presented and discussed. The retreat was particularly geared towards the development of new ideas and projects for the Cluster's renewal proposal and a possible second period of funding from 2026 – 2032. Finally, a total of 16 *liv*MatS colloquia, with external guest speakers, offered the *liv*MatS community ample opportunity to discuss current developments in their field with renowned international researchers, covering a wide range of topics and disciplines.

The Cluster has further consolidated its activities within the *Convergence Center for Living Multifunctional Material Systems* (LiMC²) founded in 2019, uniting researchers from the Penn State University and the University of Freiburg. The eSeminar Series LIMtalks, set up in 2022, continued with further talks and exchanges in 2023. A total of five LIMC² Seed Grants were carried out in 2023. These grants allow researchers from Penn State and *liv*MatS to join forces and maximize the center's potential, adding to the cluster's research portfolio. In addition, five Penn State undergraduate students (from four different departments and two colleges) visited *liv*MatS for eight weeks in summer 2023. This was the first cohort of the new International Partnership for Responsive Infrastructure using Sustainable Multifunctional Materials (iPRISM), funded by the National Science Foundation.

Throughout 2023, *liv*MatS worked on implementing and further developing its early career advancement objectives. Five candidates were selected and hired during a two-tiered selection process for the Cluster's Agnes Pockels and Hermann Staudinger doctoral fellowship program. The Cluster's successful Master Lab program saw its fifth and sixth iterations completed in 2023. Master students (12 in winter, 17 in summer) worked independently on research ideas in various fields under the supervision of a researcher from the Cluster. A seventh iteration began in October 2023 with 11 new master students working on research challenges. A total of 74 master students will have completed the *liv*MatS Master Lab by the end of the winter term 2023/2024.

The annual *liv*MatS bootcamp took place on 24 and 25 April for the new PhDs and postdocs who joined the Cluster in 2022 and early 2023. The bootcamp provided an overview of the Cluster's key science areas and research infrastructure at FIT, as well as a first science communication training and networking possibilities among the early career researchers. In 2023, the Cluster introduced its core lecture series which serves to cover core Cluster science topics in a basic fashion for its interdisciplinary group of researchers collaborating across numerous disciplines. Five core lectures were held in 2023 with more planned for 2024. The new PhDs and postdocs also received mandatory G*ood Scientific Practice* training, voluntary workshops on *Project-Time Management, Student Supervision*, and *Data Management with Chemotion ELN*, while first generation PhDs had a workshop on *Argumentation and Presentation Skills for Thesis Defense*. Under the umbrella of Gender & Diversity, early career researchers had half day workshops on *Anti-bias training* and *Resilience in research*. The Writer's Studio launched a four-week "Writing in the Sciences" (WiTS) program for new researchers, offering a comprehensive, practice based course covering the foundations of scientific writing. The course was well received (8.6/10 rating) and had 17 participants. For seasoned researchers, Golden Days of writing returned for regular meetings (17 in total).

In 2023, the Intellectual Property Management carried out a comprehensive and detailed benchmarking of the Cluster's performance.

This internal assessment compared the Cluster's success with the goals and performance indicators set out in the original proposal and compared its progress with that of international competitors. Additionally, knowledge mapping was performed according to the general categories of the Web of Science. The main knowledge categories were also used for scientific benchmarking in relation to the citation impact for the period between 2019 and 2023. A comparative benchmark value was obtained by evaluating the same category or topic in the same period for e.g. different institutes or only for DFG-funded publications. The Intellectual Property Management also evaluated and supported several invention disclosures resulting from *liv*MatS Cluster findings.

Fig. 2: Exterior of the *liv*MatS Biomimetic Shell @ FIT. © ICD/ITKE/IntCDC Universit of Stuttgart, Photo: Conné van d'Grachten.

After completing the *liv*MatS Pavilion in the Botanic Garden in 2021, the Cluster's second pavilion project gained momentum in 2022 and 2023. The *liv*MatS Biomimetic Shell @ FIT is a building demonstrator designed and realized by researchers from the Cluster of Excellence "Integrative Computational Design and Construction for Architecture" (IntCDC) at the University of Stuttgart. Scientists from IntCDC and *liv*MatS will develop and research sustainable materials and alternative construction methods using the building in the future. After the roofing ceremony in December 2022, the *liv*MatS Biomimetic Shell @ FIT was officially inaugurated in June 2023. Located in close proximity to the FIT, the biomimetic building shell measures 345-square-meter and is designed as a lightweight construction. The shell's 127 hollow cassettes made of wood were robotically manufactured and inspired by the modular skeleton of the sea urchin.

*liv*MatS has also been involved in several outreach events this year. For the fourth time, *liv*MatS took part in the "Science Days" at Europapark Rust from October 19 to 21, 2023. At the *liv*MatS booth, more than 10.000 visitors of Germany's biggest science festival were able to try out for themselves how hydrophobic surfaces or metamaterials behave, learn why thermoresponsive plastics change color, and how soft robot elements work. Also in October, journalists from the "Wissenswerte", Germany's largest science journalism conference, visited *liv*MatS. During a tour of the Cluster's Shared Laboratories, they were given an overview of the Cluster's research and were able to ask the scientists questions about their areas of expertise. In addition, the Cluster offered guided tours of the Botanic Garden of the University of Freiburg for school groups, teachers and professionals, implementing the *liv*MatS outreach concept "Learning from Nature in Nature". In these tours, the groups gained insight into the idea behind the *liv*MatS Pavilion and the Cluster's biomimetic research. In May 2023, *liv*MatS and the Freiburg "Creative Mornings" network jointly organized a lecture event in the *liv*MatS Pavilion, where interested members of the public could learn more about the research on cognitive affective maps in Research Area D from *liv*MatS doctoral researcher Sabrina Livanec. The Cluster also welcomed female students for a "Girls Day" event. Together with the group of *liv*MatS Principal Investigator Céline Calvino, the students prepared different types of polymer materials in the lab and anlayzed them qualitatively. At the end of the year, politicians from the Municipal Council Freiburg visited the *liv*MatS Biomimetic Shell @ FIT to discuss the topic of sustainable construction with *liv*MatS researchers at a "Parlamentarischer Abend" ("Parliamentary Evening").

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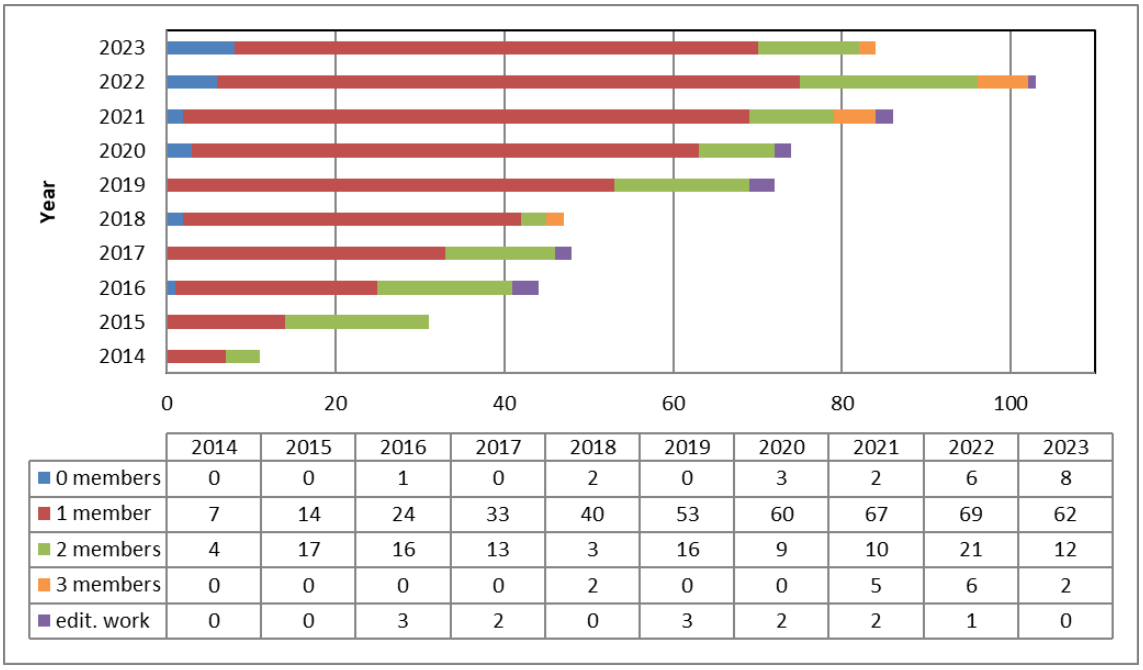
PUBLICATIONS

The publications are automatically assigned to the individual institutes of the University of Freiburg according to the affiliation stated in the original publication. In case of discrepancies, we have corrected them in Freidok plus to the best of our knowledge.



	2014	2015	2016	2017	2018	2019	2020	2021	2022	2023
0 members	0	0	1	0	2	0	3	2	6	8
1 member	7	14	24	33	40	53	60	67	69	62
2 members	4	17	16	13	3	16	9	10	21	12
3 members	0	0	0	0	2	0	0	5	6	2
edit. work	0	0	3	2	0	3	2	2	1	0

Fig. 1: Peer-reviewed publications and editorial work from 2014 until 2023

PEER-REVIEWED PUBLICATIONS

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Heizmann, Philipp Alexander: Fantastic nanoparticles and where to find them: advanced electron microscopy for the investigation of novel electrocatalysts, 2023. [Supervisor: Vierrath, Severin; Reviewer: Vierrath, Severin; Second reviewers: Fischer, Anna; Zengerle, Roland] https://doi.org/10.6094/UNIFR/239557

Hoenders, Daniel: Photochemical engineering of soft materials, 2023. [Supervisor: Walther, Andreas; Reviewer: Walther, Andreas; Second reviewer: Barner-Kowollik, Christopher] https://doi.org/10.6094/UNIFR/241377

Hu, Qiwei: Atomic force microscopy based characterization of functional interfaces, 2023. [Supervisor: Hugel, Thorsten; Second reviewers: Pastewka, Lars; Koslowski, Thorsten] https://doi.org/10.6094/UNIFR/235974

Jentzsch, Maximilian: Zitrusfrüchte als biomimetische Inspiration für technische Materialsysteme – Funktionsmorphologische und biomechanische Charakterisierung ausgewählter Zitrusfruchtschalen, 2023. [Supervisor: Speck, Thomas; Reviewer: Speck, Thomas; Second reviewers: Eberl, Christoph; Dondl, Patrick] https://doi.org/10.6094/UNIFR/243507

Klimm, Frederike (2023): Natural Coil Springs: Biomechanics, Functional Morphology and Anatomy of Passion Flower Tendrils. [Universitity of Freiburg; supervisor: Speck T, Thielen, M].

Koch, Susanne: Electrode engineering for anion-exchange membrane water electrolyzers, 2023. [Supervisor: Vierrath, Severin; Reviewer: Vierrath, Severin; Second reviewer: Glunz, Stefan] https://doi.org/10.6094/UNIFR/234205

Kolb, Simon: Electrochemical activation of strained donor-acceptor substituted carbocycles and selective hydrogenation of benzylic olefins by electroreduction, 2023. [Supervisor: Werz, Daniel B.; Reviewer: Brückner, Reinhard; Second reviewer: Krossing, Ingo] https://doi.org/10.6094/UNIFR/240624

Kubas, Dustin: CO2 Valorization: Heteropoly Acids as Dehydration Catalysts in Direct DME Synthesis, 2023. [Supervisors: Krossing, Ingo; Fischer, Anna; Reviewer: Krossing, Ingo; Second reviewer: Fischer, Anna] https://doi.org/10.6094/UNIFR/233279

Ma, Jiahui: Photocages, photocaged nucleotides and subcellular delivery, 2023. [Supervisor: Jessen, Henning; Reviewer: Jessen, Henning; Second reviewer: Rapp, Bastian Ernst] https://doi.org/10.6094/UNIFR/238833

Maftuhin, Wafa: Aspect of mechanochemistry and donor-acceptor polymers: insight from theory and simulation, 2023. [Supervisor: Walter, Michael; Reviewer: Dzubiella, Joachim; Second reviewer: Reiter, Günter] https://doi.org/10.6094/UNIFR/243208

Mees, Jan: Self-mated hydrogel friction, 2023. [Supervisor: Pastewka, Lars; Reviewer: Dzubiella, Joachim] https://doi.org/10.6094/UNIFR/236615

Meßmer, Marius: Development and characterization of resource-saving doping processes for industrial silicon solar cells, 2023. [Supervisor: Glunz, Stefan; Reviewer: Glunz, Stefan; Second reviewer: Kray, Daniel] https://doi.org/10.6094/UNIFR/238628

Möller, Martin (2023): Entwicklung eines mehrstufigen Methodenrahmens für eine prospektive Nachhaltigkeitsbewertung von neuartigen Technologien und Materialsystemen (TAPAS). [PhD thesis, Universitity of Freiburg; supervisors: Speck T, Grieshammer R (Ökoinstitut Freiburg & Exzellenzcluster livMatS].

Sanner, Antoine: How surface roughness affects adhesion, 2023. [Supervisor: Pastewka, Lars; Reviewer: Pastewka, Lars; Second reviewer: Müser, Martin H.] https://doi.org/10.6094/UNIFR/235048

Schmidt, Alexei: Development and analysis of new liquid electrolytes from abundant metals for battery application, 2023. [Supervisor: Krossing, Ingo; Reviewer: Krossing, Ingo; Second reviewer: Kurz, Philipp]

Schmitt, Manuel: Investigation of novel transition metal carbonyl cations and dinitrogen complexes, 2023. [Supervisor: Krossing, Ingo; Reviewer: Krossing, Ingo; Second reviewer: Kurz, Philipp]

Shaner, Sebastian: On-chip bioelectronic platforms for direct current stimulation of single cells, cell collectives, and tissues, 2023. [Supervisor: Asplund, Maria; Reviewer: Asplund, Maria; Second reviewer: Rapp, Bastian E.] https://doi.org/10.6094/UNIFR/237338

Wei, Wei: Theoretical atomic-scale modelling of perovskite-type photo-battery materials, 2023. [Supervisor: Elsässer, Christian; Reviewer: Elsässer, Christian; Second reviewer: Moseler, Michael] https://doi.org/10.6094/UNIFR/241705

Zeng, Zhiqiang: Template-assisted design of 0D and 1D nanomaterials for efficient photoelectroand electrocatalytic water splitting, 2023. [Supervisor: Fischer, Anna; Reviewer: Kurz, Philipp; Second reviewer: Roth, Christina] https://doi.org/10.6094/UNIFR/238127

Diploma, Master, Bachelor and State Examination Theses

Auth, Philipp (2023): Towards autonomous pneumatic soft robots: Design and fabrication of a 3D-printed, bioinspired walker with sensing abilities. [Master of Education, Master thesis, University of Freiburg; supervisors: Tauber F, Speck T].

Eckert, Rahel (2023): Leaf unfolding in Nymphaea caerulea (Nymphaeaceae): Characterization of leaf ontogeny and anatomy. [Bachelor thesis, University of Freiburg; supervisors: Modert M, Speck T].

Enuloe, Jonas (2023): Natural gaits to inspire a soft pneumatic leg for a soft robotic walker. [Bachelor thesis, University of Freiburg; supervisors: Teichmann J, Tabuer, F, Speck T].

Gentner, Lukas (2023): Biomechanische Charakterisierung des Öffnungsverhaltens und der Materialermüdung von Kiefernzapfenschuppen (Pinus jeffreyi). [Bachelor thesis, University of Freiburg; supervisors: Masselter T, Ulrich K, Speck T].

Groth, Johanna (2023): Development and optimization of a microfluidic CRISPR/Cas-based assay for target-amplification-free nucleic acid detection. [Master thesis, University of Freiburg; supervisor: Dincer, C.]

Homburger, Jaro (2023): Untersuchungen der Beinmorphologie und des Öltransfers von Macropis europaea. [Master thesis, University of Freiburg; supervisors: Gallenmüller F, Speck T].

Klasen Teresa (2023): Die Rankenspiralisierung der Passiflora caerulea: Funktionelle Morphologie. [Bachelor thesis, University of Freiburg; supervisors: Klimm F, Speck T].

Kürner, Lukas (2023): Charakterisierung bioinspirierter, softrobotischer Pneumatik-Aktuatoren für Greifer mit passiven Haltemechanismen. [Master thesis, University of Freiburg; supervisors: Tauber F, Speck T].

Rützler, Alex (2023): Investigation of mesoporous N-doped carbon nano-spheres as anode materials for sodium ion batteries. [Master thesis, University of Freiburg; supervisors: Fischer A, Büttner, J].

Schäfer, Simon (2023): Biomechanische Charakterisierung des Öffnungsverhaltens und der Materialermüdung von Kiefernzapfen (Pinus nigra und Pinus jeffreyi). [Bachelor thesis, University of Freiburg; supervisors: Masselter T, Speck T].

Wiese, Lukas (2023): Untersuchung der frühen Mistelkeimling-Wirts-Interaktion (Viscum album). [Bachelor thesis, University of Freiburg; supervisors: Mylo M, Speck T].

Yoshida, Sun (2023): Development of a thermoresponsive shape memory multilayer bioinspired Venus flytrap demonstrator. [Master thesis, University of Freiburg; supervisors: Tauber F, Speck T].

FIT COLLOQUIUM 2023

Kolloquium 2023

Dienstag 10. Oktober 2023 / FMF und FIT

09:00	Bernd	Rolauffs	Molecular effectivity and model-based importance of engineering cell geometric features for controlling human chondrocyte phenotype via micro-patterning: a multivariate modeling-based and subspace clustering analysis
09:15	David	Böcherer	COLOR3D – Multicolored 3D printing of wood composites
09:30	Franziska	Dreher	TriboChem – Chemistry of Triboelectric Materials
09:45	Sima	Heidari	Atomic Layer Deposition of Titanium Oxide over Mesoporous Nitrogen-doped Carbon
10:00	Michael	Moseler	Classical molecular dynamics of strongly driven non-equilibrium systems – from exploding nanoclusters to collapsing nanotubes
10:15	**Kaffeepause**		
10:30	Laura	Hartmann	Functional and adaptive polymer materials for biomedical and biotechnological applications
10:45	Aljoscha	Baumann	Atomistic analysis of volume changes in tungsten-bronze-type compounds A_xFeF_3 during intercalation of A cations (A=Li, Na, K)
11:00	Gerardo	Roque	Medipix Spectra and Spatial Resolution Simulations for Dense Breast/Implant Mammography
11:15	Isabella	Fiorello	Plant-inspired hybrid microfabricated machines
11:30	Prasanth Babu	Ganta	Wetting Effects on Rough surfaces using Molecular Dynamics Simulations
11:45	**Kaffeepause**		
12:00	Jürgen	Rühe	Water-Based Lubricants for Extremely Efficient Lubrication
12:15	Max	Mylo	Digital image correlation as an optical technique for strain and deformation measurements: requirements, possibilities, limitations and the possibility of underwater analysis
12:30	Luca	Bohn	Integrated reference electrodes for CO^2 electrolysis cells
12:45	Anna	Fischer	Ultrahigh Mass Activity Pt Entities composed of Pt Single atoms, Clusters and Nanoparticles on Mesoporous N-doped Carbon Nanospheres for improved Hydrogen Evolution Reaction
13:00	Niloofar	Nekoonam	Photoswitchable porous substrates for on demand wetting patterns creation
13:15	**Mittagessen**		

Kolloquium 2023

14:30	Khaled Josephine	Seteiz Häberlein	Carbon black supported Ag NPs for CO^2 electrolysis to CO
14:45	Falk	Tauber	Thermoresponsive artificial Venus Flytrap demonstrators
15:00	Sebastian	Kluck	Replikative Herstellung von Metallformen für die Polymerreplikation mit geringer Oberflächenrauheit
15:15	S. Esmael	Balaghi	Application of In-situ Electrochemical Liquid (Scanning) Transmission Electron Microscopy in understanding Materials Dynamics under Electrochemical Conditions
15:30		**Kaffeepause**	
15:45	Gopakumar	Sivasankarapillai	Formaldehyde and Isocyanate Free 'Class A1' wood Adhesive from wood Tannin
16:00	Santiago	Franco Corredor	Binary fused silica glass-stacking system for optical waveguides
16:15	Silvio	Tisato	Material characterization and optimization for Volumetric 3D Printing
16:30	Richard	Prediger	High-resolution structuring of transparent polycrystalline spinel ceramics
16:45	Peilong	Hou	Digital Light Processing-Based Fabrication of Ligand Micropatterns on High-Density Antifouling PEG Brushes
17:00		**Ende**	
17:30		**Direktoriumssitzung FIT**	
19:00		**Abendessen** (für angemeldete TN)	

Kolloquium 2023

Mittwoch 11. Oktober 2023 / FIT

09:00	Edoardo	Milana	Physical Control of Soft Robots
09:15	Karima	Saddedine	Bi-O-ACTUATOR: Bio-inspired Hydraulic Actuator on Wood-Basis
09:30	Joel	Monti	[2+2]-photocycloadditions of coumarin derivative as an effective tool for the reversible formation of covalent bonds – Towards the design of renewable polymer materials
09:45	Yu	Wang	LiNi0.6Mn0.2Co0.2O2 (NMC622) Symmetric Cells for Mode II Integrated Photobattery
10:00	David	Schwarz	Mechanical metamaterials with incorporated capsules for advanced functionalities
10:15	**Kaffeepause**		
10:45	Yashika	Gupta	Development of Evaporated All-inorganic Perovskite for Tandem Solar Cell Applications
11:00	Jana	Stumpp	Mechanically-Induced Debonding of Adhesive Capsules based-Composites
11:15	Christoph	Lehmann	Gallisense: Giving materials the passive ability to sense
11:30	Sunel	de Kock	NEXAFS spectra of model sulfide chains
11:45	Mahesh	Pol	Abiotic Phosphate fueled non-equilibrium self-assembly
12:00	**Mittagspause mit Snack**		
12:45	Mehmet-Talha	Yapa	Photo Crosslinking Hydroxypropyl Cellulose (HPC) and Organosolv Lignin (OSL) for 3D Printing: A Comparative Kinetic Study with Chemically Modified HPC and OSL
13:00	Juliane	Borchert	Perovskite Silicon Tandem and Triple Solar Cells – Progress and Challenges
13:15	Michelle	Modert	Leaf unfolding - Similarities and differences in peltate leaves from different habitats
13:30	Cong	Tao	Computational investigation of layered halide perovskites for mode III photobatteries
13:45	**Ende des Kolloquiums**		

IMPRESSUM

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