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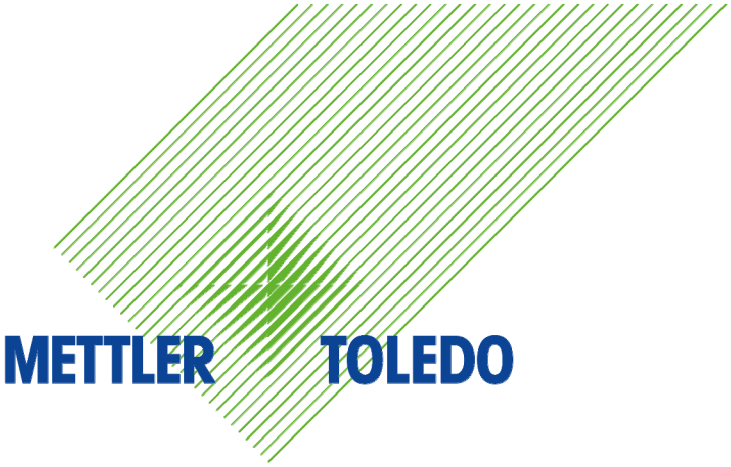

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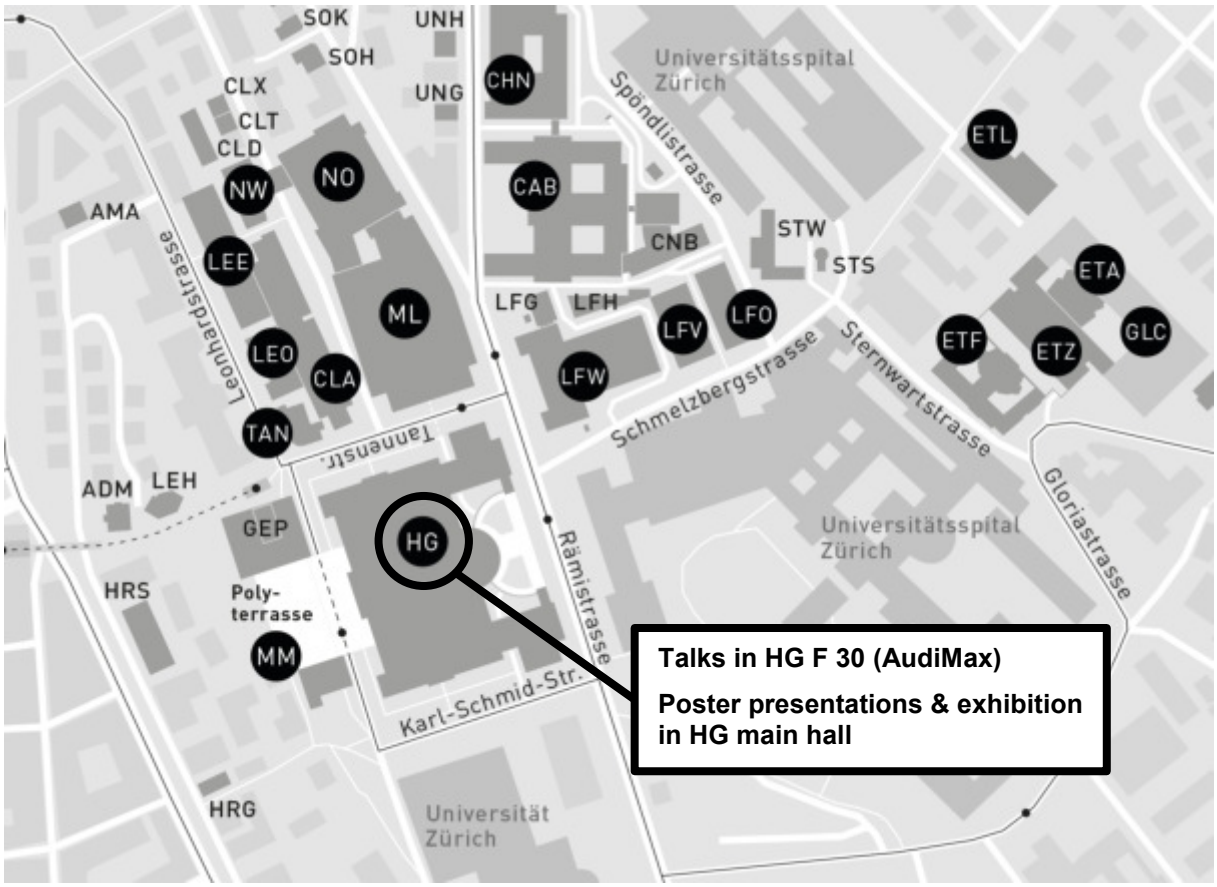

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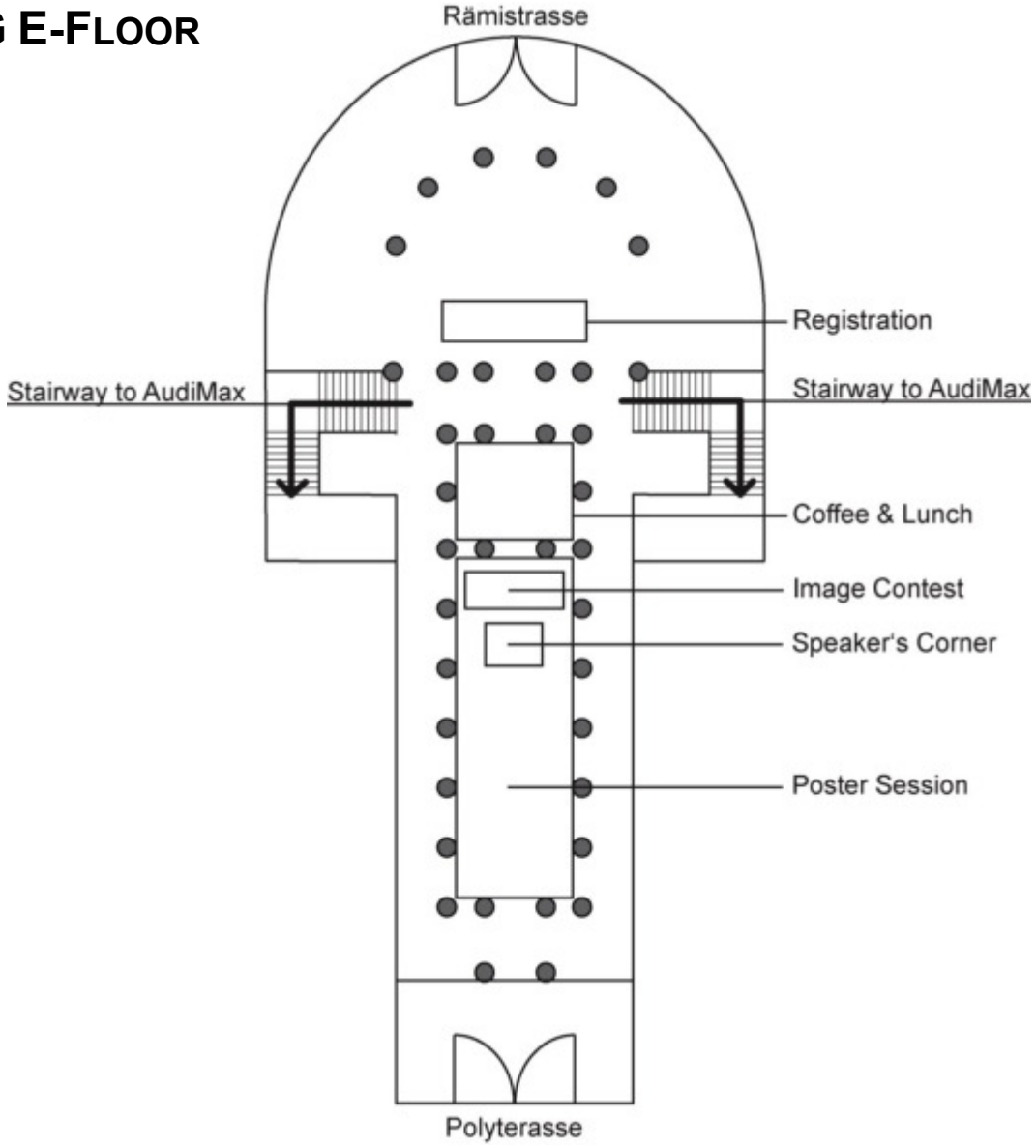

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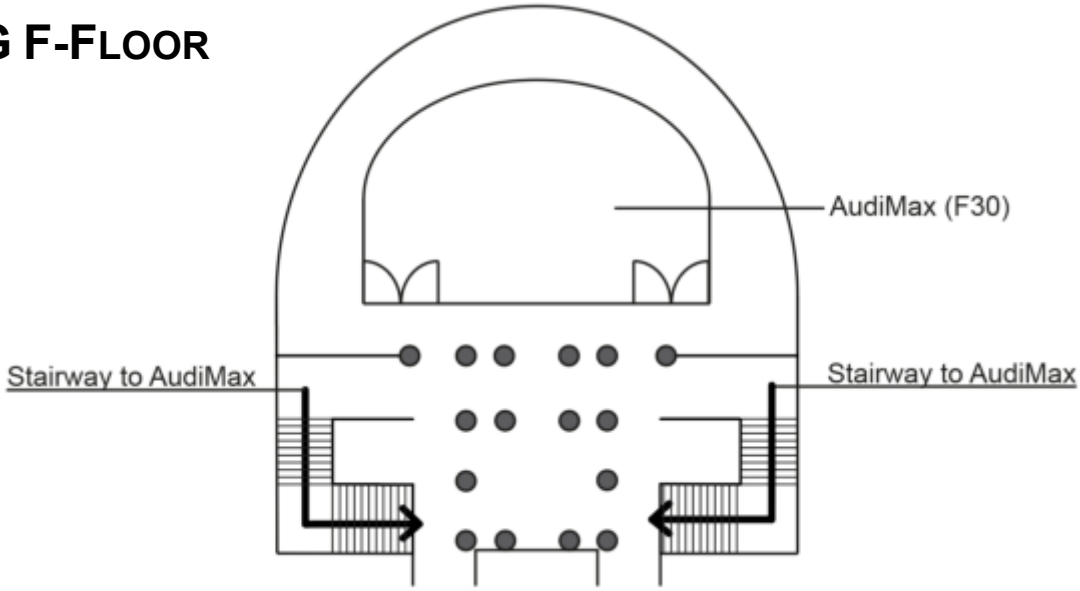

PROGRAM

08.00	*Registration*
08.50	**Prof. André R. Studart,** *MaP Director* Opening remarks
09.00	**Elia A. Guzzi,** *Macromolecular Engineering, D-MAVT* Universal Nanoparticle-Based Ink for Biomaterials Additive Manufacturing
09.12	**Murielle Schreck,** *Multifunctional Materials, D-MATL* The Beauty Behind Hydrogen Production – Titania Nanoparticle-based Aerogels as Photocatalysts
09.24	**Michael Gerlt,** *Mechanics & Experimental Dynamics, D-MAVT* High Throughput Continuous Cell Secretome Separation Inside Microscale Droplets by Means of Acoustophoresis
09.36	**Laura Piveteau,** *Functional Inorganic Materials, D-CHAB* Atomistic Insights Into the Structure of Colloidal Semiconductor NC Using Advanced NMR Spectroscopy
09.48	**Pitches by:** **Cyprien Hoelzl,** *Structural Mechanics & Monitoring, D-BAUG* Data-Empowered Assessment of Railway Infrastructure **Nadine Lobsiger,** *Functional Materials Laboratory, D-CHAB* A S. Cerevisiae-Based Biosensor Material for the Detection of Endocrine-Disrupting Chemicals: Reliability, Stability and Analysis of Environmental Samples **Oleg Testoni,** *Composite Materials & Adaptive Structures, D-MAVT* A Novel Concept of Shape-Adaptable Sandwich Panel with Shape Memory Alloy Actuators
10.00	*Coffee Break & Poster Session*
11.00	**Paolo Testa,** *Mesoscopic Systems, D-MATL & PSI* Magnetically Addressable Shape-memory and Stiffening in a Composite Elastomer
11.12	**Marion Frey,** *Wood Materials Science, D-BAUG & Empa* Tunable Wood and Design of High-performance Cellulose Fiber Materials
11.24	**Konstantin Schulz-Schönhagen,** *Functional Materials Laboratory, D-CHAB* Continuous Production of a Shelf-stable Living Material as a Biosensor Platform
11.36	**Aurelio A. Rossinelli,** *Optical Materials Engineering, D-MAVT* Highly Luminescent Colloidal Core/Shell Nanoplatelets with Graded Shell Composition
11.48	**Pitches by:** **Peter Benedek,** *Materials & Device Engineering, D-ITET* Surface Phonons in Li Ion Battery Cathode Materials **Alain Reiser,** *Nanometallurgy, D-MATL* Electrohydrodynamic Redox 3D Printing: Chemically Architected Metals at the Submicron Scale **Raphael Brechbühler,** *Optical Materials Engineering, D-MAVT* Dark Optical Modes on Periodically Patterned Plasmonic Films
12.00	*Lunch & Poster Session*

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13.45	**Dr. Nicolas Broguière,** *Tissue Engineering & Biofabrication, D-HEST* Engineering of Synthetic Extracellular Matrix Analogues Supporting and Guiding Neurons
14.05	**Dr. Vladimir Paunović,** *Advanced Catalysis Engineering, D-CHAB* Catalytic Processes for Natural Gas Valorization via Bromine Chemistry
14.30	*Coffee Break*
15.15	**Matthias Haug,** *Complex Materials, D-MATL* Cold Sintering – A New Ceramic Processing Route, Investigated Using In-Situ X-Ray Synchrotron Tomography
15.27	**Mario Arcari,** *Food & Soft Materials, D-HEST* Nanostructural Properties and Twist Periodicity of Cellulose Nanofibrils with Variable Charge Density
15.39	**Oksana Dudaryeva,** *Macromolecular Engineering, D-MAVT* Biophysical Regulation of Single Cell Fate in 3D
15.51	**Hendrik Th. Spanke,** *Soft & Living Materials, D-MATL* Dynamics of Membrane Wrapping of Microparticles
16.03	**Tian Tian,** *Interface & Surface Engineering of Nanomaterials, D-CHAB* Two-Dimensional Materials as High-Pass Filter of van der Waals Interactions
16.15	Flash Poster Presentations
16.30	**My Story: Science Translated to Meaningful Applications** with Michele Magno (Mithras), Gabriel Puebla-Hellmann (QZabre) & Mariia Timofeeva (PolarNon)
17.00	Industry Presentations by **avantama, BASF, Hilti, Mettler Toledo, Siga & SuSoS**
17.20	Award Ceremony
17.50	*Industry Apéro Riche*

ABSTRACTS OF TALKS

Session 1: 09.00 – 10.00

Chair: Prof. David Norris (Optical Materials Engineering, D-MAVT)

Universal Nanoparticle-Based Ink for Biomaterials Additive Manufacturing

Elia A. Guzzi, Giovanni Bovone, and Mark W. Tibbitt
Macromolecular Engineering, D-MAVT, ETH Zurich

The Beauty behind Hydrogen Production – Titania Nanoparticle-Based Aerogels as Photocatalysts

Murielle Schreck[1], Manuel Bertsch[1], Nicole Kleger[2], and Markus Niederberger[1]
[1] Multifunctional Materials, D-MATL, ETH Zurich, [2] Complex Materials, D-MATL, ETH Zurich

Our planet is struggling with climate change and an increasing demand of energy. Two problems, one solution: the abundantly available energy of the sun needs to be harnessed and used to produce renewable energy sources. Hydrogen is a good alternative to fossil fuels. Its production via photocatalytic processes converts solar energy into chemical energy [1].

Here, we present titania nanoparticle-based aerogels for photocatalysis at the gas-solid interface producing hydrogen out of the vapor phase of a water-methanol mixture.

Using aerogels with their large surface areas and high open porosity greatly increases the interaction between gas and photocatalyst compared to powders and thin films [2,3].

Titania is the most reliable photocatalytic material due to its stability, non-toxicity, and low cost. However, the fast electron-hole recombination and the photocatalytic activity only in the UV range prevent hydrogen production rates of more than some micromole per gram of photocatalyst and hour of illumination (µmol/(g×h)).

By fabricating our aerogels with a bottom-up approach from pre-synthesized nanoparticles as building blocks, we can easily combine different materials and nanostructures within one monolith. The incorporation of metal co-catalysts like palladium nanoparticles into the titania aerogels results in a significant improvement of the photocatalytic activity. The metal nanoparticles trap the photocatalytically-generated electrons and, therefore, provide a spatial separation for the charge carriers and prevent their recombination [1]. More than 200 times higher hydrogen production rates could be measured in the titania-palladium system (with a maximum rate of 1035 µmol/(g×h)) compared to the co-catalyst-free titania system.

[1] M. Schreck and M. Niederberger, *Chem. Mater.* **31**, 597 (2019). [2] F. Rechberger and M. Niederberger, *Nanoscale Horiz.* **2**, 6 (2017). [3] F. Rechberger and M. Niederberger, *Mater. Horiz.* **4**, 1115 (2017).

High Throughput Continuous Cell Secretome Separation Inside Microscale Droplets by Means of Acoustophoresis

Michael Gerlt[1], Dominik Haidas[2], Alexandre Ratschat[1], Philipp Suter[1], Petra Dittrich[2], and Jürg Dual[1]
[1] Mechanics & Experimental Dynamics, D-MAVT, ETH Zurich, [2] Bioanalytics, D-BSSE, ETH Zurich

Atomistic Insights into the Structure of Colloidal Semiconductor NC using Advanced NMR Spectroscopy

Laura Piveteau[1], Dmitry Dirin[1], Christopher P. Gordon[1], Ta-Chung Ong[1,3], Brennan J. Walder[2], Aaron J. Rossini[3,4], Lyndon Emsley[3], Christophe Coperet[1], and Maksym V. Kovalenko[1,2]

[1] Functional Inorganic Materials, D-CHAB, ETH Zurich and Empa, [2] Laboratory of Magnetic Resonance, ISIC, EPF Lausanne, [3] Department of Chemistry and Biochemistry, University of California Los Angeles, [4] Department of Chemistry, Iowa State University

Semiconductor nanocrystals (NCs) are a highly versatile class of materials, whose colloidal synthesis allows for a precise control over their composition, size, shape and hence properties, such that they have been integrated into numerous devices, including solar cells, transistors, photodetectors, etc. Despite its large impact on optoelectronic properties, the exquisite atomistic understanding of the NC structure – especially the surface structure – has remained elusive. The intrinsic lack of translational symmetry in NCs and the high atomic disorder limit the insight from the X-ray diffraction, which is usually the working horse for structural elucidation.

Nuclear magnetic resonance (NMR) spectroscopy is highly sensitive to the local chemical and electronic structure and does not pose any requirements to the crystallinity of the samples. However, large degrees of disorder will lead to broad signals and crowded NMR spectra. But the major limitation to the study of semiconductor NCs with NMR so far was the inherently low sensitivity NMR spectroscopy, which is exacerbated for inorganic nuclei.

We have found that the NMR signal enhancing method dynamic nuclear polarization (DNP) can be adapted to colloidal samples and that 2D correlation spectroscopy can increase spectral resolution such that chemical, structural, morphological and topological information about the core and the surface of semiconductor NCs become readily accessible.

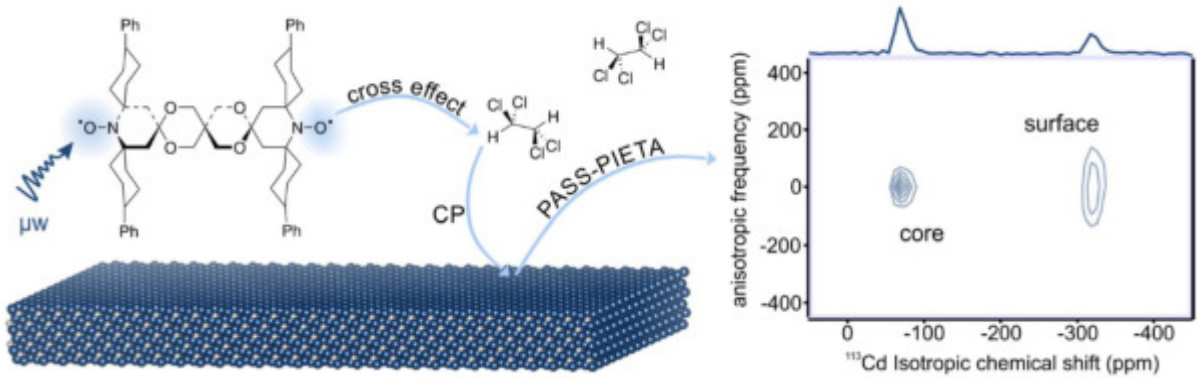


Fig.: Polarization transfer mechanism of DNP-NMR (left) to colloidal zincblende CdSe nanoplatelets and the latter's DNP enhanced PASS-PIETA spectrum (right) resolving the surface and core species.

Data-Empowered Assessment of Railway Infrastructure

Cyprien Hoelzl[1], Vasilis Dertimanis[1], Dorothea Winklehner[2], Simon Züger[2], and Eleni Chatzi[1]

[1] Structural Mechanics & Monitoring, D-BAUG, ETH Zurich, [2] Infrastruktur – Anlagen & Technologie – Fahrweg (I-AT-FW), SBB Bern

A S. Cerevisiae-Based Biosensor Material for the Detection of Endocrine-Disrupting Chemicals: Reliability, Stability and Analysis of Environmental Samples

Nadine Lobsiger[1], Jonathan E. Venetz[2], and Wendelin J. Stark[1]

[1] Functional Materials Laboratory, D-CHAB, ETH Zurich, [2] Experimental Systems Biology, D-BIOL, ETH Zurich

A Novel Concept of Shape-Adaptable Sandwich Panel with Shape Memory Alloy Actuators

Oleg Testoni[1], Sampada Bodkhe[1], Andrea Bergamini[2], and Paolo Ermanni[1]
[1] Composite Materials & Adaptive Structures, D-MAVT, ETH Zurich and Empa, [2] Laboratory Acoustics / Noise Control, Empa

Shape memory alloys (SMA) are well known for the high stress and the large stroke that they can achieve simultaneously and, therefore, have been widely used as actuators in different shape-adaptable structures. While most of the adaptive structures found in the literature using SMAs as actuators have been designed to accomplish only a single type of deformation, we present in this work a novel structural concept able to achieve multiple shapes. The concept consists of a modular sandwich panel composed of rigid cells connected by active joints hosting SMA wires, which are used as actuators. Thanks to their geometry, the joints act both as stroke amplification systems and as bias springs, allowing for multiple actuations of one-way SMA wires. The active joints are placed in pairs both on the upper and on the lower face sheet of the panel and control the distance as well as the orientation of neighbouring panel cells. As a result, it is possible to deform the panel both in-plane and out-of-plane. In this paper, we present the working principle of the proposed concept and of its actuation system. The mechanical behaviour of the active joints is investigated both numerically and experimentally and the results obtained are implemented in a finite element model of the shape-adaptable sandwich panel. Four actuation strategies of the active joints are investigated and the achieved deformations returned by the corresponding simulations are compared with the experimental measurements carried out on a demonstrator.

Fig.: Presented concept of shape-adaptable sandwich panel.

Session 2: 11.00 – 12.00

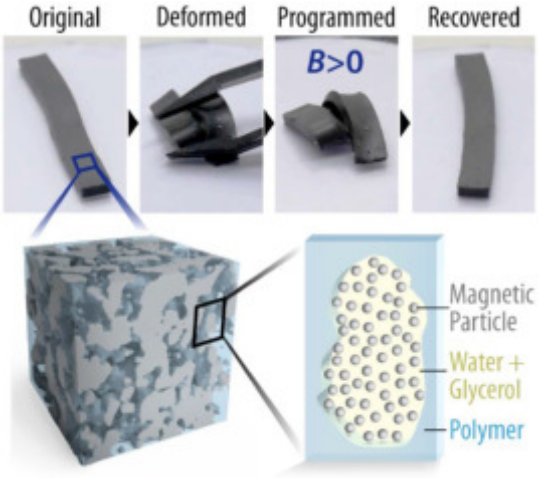
Chair: Prof. Rachel Grange (Optical Nanomaterials, D-PHYS)

Magnetically Addressable Shape-Memory and Stiffening in a Composite Elastomer

Paolo Testa[1,2,3], Robert W. Style[2], Jizhai Cui[1,3], Claire Donnelly[1,3], Elena V. Borisova[4], Peter M. Derlet[5], Eric R. Dufresne[2], and Laura J. Heyderman[1,3]

[1] Mesoscopic Systems, D-MATL, ETH Zurich and PSI, [2] Soft & Living Materials, D-MATL, ETH Zurich, [3] Multiscale Materials Experiments, PSI [4] TOMCAT Beamline, PSI [5] Condensed Matter Theory Group, PSI

With a specific stimulus, shape-memory materials can assume a temporary shape and subsequently recover their original shape, a capability that renders them relevant for applications in fields such as biomedicine, aerospace and wearable electronics. Shape-memory in polymers and composites is usually achieved by exploiting a thermal transition to program a temporary shape and successively recover the original shape. This may be problematic for heat sensitive environments and when rapid and uniform heating is required. In this work, a soft magnetic shape-memory composite is produced by encasing liquid droplets of magneto-rheological fluid into a polydimethylsiloxane matrix. Under the influence of a magnetic field, this material undergoes an exceptional stiffening transition, with an almost 30-fold increase in shear modulus. Exploiting this transition, fast and fully reversible magnetic shape memory is demonstrated by embossing, by simple shear and by unconstrained three-dimensional deformation. Using advanced synchrotron x-ray tomography techniques, the internal structure of the material is revealed and correlated with the composite stiffening and shape-memory mechanism. Based on a simple emulsion process, this material concept can be extended to different fluids and elastomers, and can be manufactured with a wide range of methods [1].



[1] P. Testa, et al., *Advanced Materials* (in press).

Tunable Wood and Design of High-Performance Cellulose Fiber Materials

Marion Frey[1,2], Meri Zirkelbach[3], Clemens Dransfeld[4], Tobias Keplinger[1,2], and Ingo Burgert[1,2]

[1] Wood Materials Science, D-BAUG, ETH Zurich, [2] WoodTec, Laboratory for Cellulose & Wood Materials, Empa, [3] Design and Arts, Lucerne University of Applied Sciences and Arts, [4] Aerospace Engineering, Delft University of Technology

The development of materials with controlled hierarchy, as common for many biological materials, is one of the main challenges in materials science. A promising way to directly profit from natures design principles is to use and modify biological materials in top-down processes. Wood, for example, can be turned into a versatile engineering material by removing the inherent matrix (lignin) followed by densification [1]. The densified cellulose material possesses tunable tensile stiffness values between 5 GPa and 30 GPa and tensile strength values between 80 MPa and 250 MPa, depending on the degree of densification. In addition to the excellent mechanical properties, delignified wood materials can be optimized towards external loading conditions by simple fiber alignment adjustments in wet state [2].

The manufacturing of densified 3D parts, however, is rather challenging until now. Formability prerequisites free water in between cells. But in this state, delignified wood can be hardly densified with standard processing techniques. Water in between fibers creates a counter pressure, which leads to reduced densification, cracks and distortions in the fiber alignment.

In this presentation, we demonstrate our novel open-molding process to manufacture cellulose composites based on wood in a scalable way. This method allows to combine densification and shaping in a one-step process and will facilitate new design strategies for manifold application areas such as automotive industry or aviation.

[1] M. Frey, et al., *ACS Appl. Mater. Interfaces*, **10**, 5030-5037 (2018). [2] M. Frey, et al., *Adv. Sci.*, 1802190 (2019).

Continuous Production of a Shelf-Stable Living Material as a Biosensor Platform

Konstantin Schulz-Schönhagen, Nadine Lobsiger, and Wendelin J. Stark
Functional Materials Laboratory, D-CHAB, ETH Zurich

The advancements made in biological engineering have led to the development of whole-cell biosensors and their successful application in diagnostics. However, due to the sensitivity of the systems, as well as the need for advanced readout devices, the use of such sensors is limited to a laboratory environment. Here we present a novel living-material biosensor platform for the diffusion-based quantification of a small molecule analyte. The platform consists of Bacillus subtilis endospores carrying a genetic reporter construct. The spores are embedded in a PVA matrix casted to a PET support material. We show that the biosensor platform can be produced continuously on a large scale. The scalable process results in a price per sensor, which is three orders of magnitude lower than the price of a comparable biological lateral flow assay. We demonstrate the performance of the biosensor platform for the quantification of isopropyl-β-D-thiogalactopyranoside and show that the readout can be performed with a 3D-printed smartphone-based device. Finally, we demonstrate that the material is stable under various environmental conditions and that it can be stored for an extended period without losing its functionality. Aforementioned progress makes the presented living-material feasible for the application by an untrained user in the field.

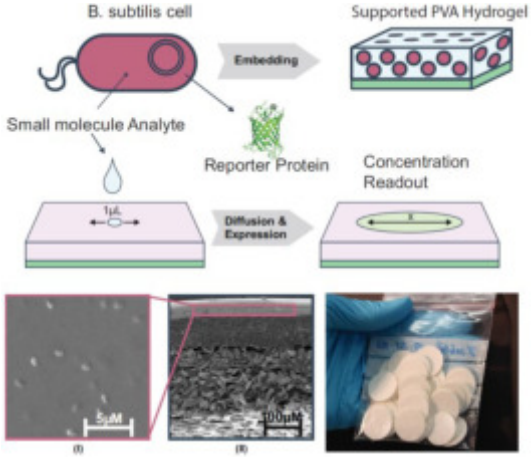


Fig.: Working principle and material demonstration of the living material biosensor.

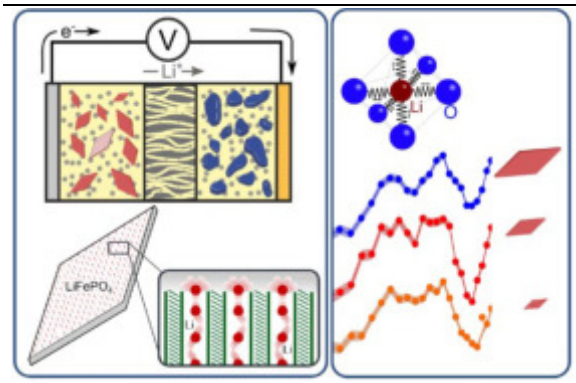
Highly Luminescent Colloidal Core/Shell Nanoplatelets with Graded Shell Composition

Aurelio A. Rossinelli, Henar Rojo, Aniket S. Mule, Marianne Aellen, Ario Cocina, Eva De Leo, and David J. Norris
Optical Materials Engineering, D-MAVT, ETH Zurich

Surface Phonons in Li Ion Battery Cathode Materials

Peter Benedek[1], Nuri Yazdani[1], Hungru Chen[2], Nils Wenzler[1], Fanni Jurànyi[3], Martin Månsson[4], M. Saiful Islam[2], and Vanessa Wood[1]
[1] Materials & Device Engineering, D-ITET, ETH Zurich, [2] Department of Chemistry, University of Bath,
[3] Laboratory for Neutron Scattering and Imaging, PSI, [4] Department of Applied Physics, KTH Stockholm

$LiFePO_4$ (LFP) is a commercial cathode material in Li ion batteries which is often used for high power applications. Typically, nanoparticles of LFP are used due to the shorter path-length for Li ions in the [010] transport direction. However, since nanoparticles have a large surface to volume ratio compared to larger micron-sized particles, the question of how the surface influences ion diffusion and charge transfer becomes relevant. Especially lattice vibrations (phonons) affect these processes by serving as a source of activation. Here, we present a method to measure and characterize (010) surface phonons in LFP by a combination of density functional theory (DFT) calculations and neutron



scattering measurements. We then extend the DFT calculations to give a prediction about the Li ion diffusivity both at the surface and in the bulk [1].

[1] P. Benedek, et al., *Sustain. Energ. Fuels* **3**, 508 (2019).

Fig.: Left: Schematic drawing of a Li ion battery with two electrodes with different materials (coloured blue and red) and a separating layer. The focus in this work lies on the interface of the electrode materials (depicted as an inset). Right: Phonon density of states of $LiFePO_4$ particles of different size in an energy range of 50 to 80meV. Image taken from [1].

Electrohydrodynamic Redox 3D Printing: Chemically Architected Metals at the Submicron Scale

Alain Reiser[1], Marcus Lindén[1], Patrik Rohner[2], Adrien Marchand[3], Henning Galinski[1], Alla S. Sologubenko[1], Jeffrey M. Wheeler[1], Renato Zenobi[3], Dimos Poulikakos[2], and Ralph Spolenak[1]

[1] Nanometallurgy, D-MATL, ETH Zurich, [2] Thermodynamics in Emerging Technologies, D-MAVT, ETH Zurich, [3] Organic Chemistry, D-CHAB, ETH Zurich

The concept of architected materials, i.e. the design of properties through architecture, is of widespread interest, e.g. for the fabrication of optical and mechanical metamaterials or advanced microelectromechanical systems. Typically, architecture is interpreted as a geometric parameter, and lattice materials with designed unit cells are the most widespread "geometrically architected" materials. However, lattices render porous materials, with absolute properties that are inferior to dense designs. Thus, we advocate for adding chemistry as a design parameter to widen the property space accessible with architected materials. For the synthesis of such “chemically architected” materials, multimaterial AM has great potential due to its voxel-by-voxel control of the chemical composition.

Here, we introduce electrohydrodynamic redox printing for the synthesis of chemically architected metals. This ink-free technique offers multi-metal printing with a chemical voxel-size of 250 nm, switching of the printed chemistry at a frequency of 10 Hz, and smallest geometrical feature size <100 nm. The underlying electrochemical principle enables as-deposited materials quality that compares well with that of PVD-deposited metals. We demonstrate the synthesis of bi-metallic Cu-Ag 3D chemical architectures that tune local reactivity or mechanical properties through deterministic design of the local chemistry [1].

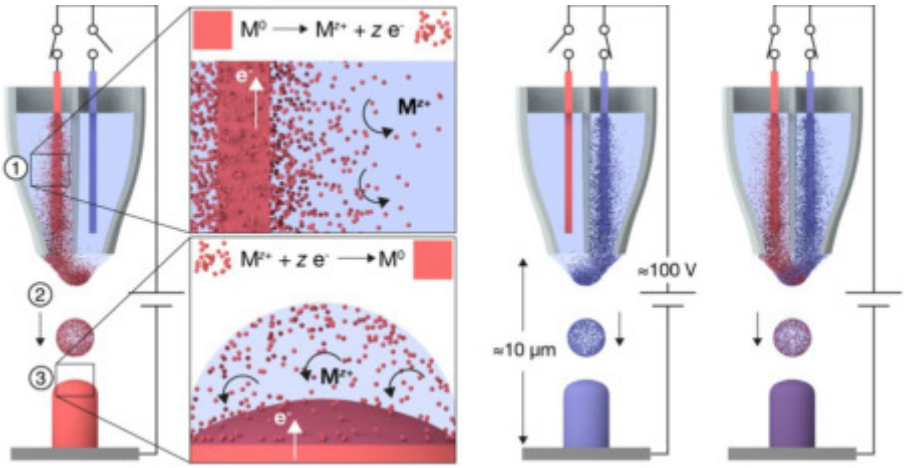


Fig.: Electrohydrodynamic redox printing: Submicron-scale multi-metal 3D printing with ions.

[1] A. Reiser, et al., *Nat. Commun.* **10**, 1853 (2019).

Dark Optical Modes on Periodically Patterned Plasmonic Films

Raphael Brechbühler[1], Sander J.W. Vonk[1,2], Nolan Lassaline[1], Freddy T. Rabouw[2], and David J. Norris[1]

[1] Optical Materials Engineering, D-MAVT, ETH Zurich, [2] Debye Institute of Nanomaterials Science, Utrecht University

MaP Award 2019
13.45 – 14.30

Chair: Prof. Petra Dittrich (Bioanalytics, D-BSSE)

Engineering of Synthetic Extracellular Matrix Analogues Supporting and Guiding Neurons

Nicolas Broguière
Tissue Engineering & Biofabrication, D-HEST, ETH Zurich

Biological tissues are highly organized. To generate the structures of complex organs such as the brain, cells must respond to an array of subtle physical and biochemical cues, which guide their behavior. Retro-engineering these microenvironments is key to provide ever more accurate in vitro models of organs in health and disease, and to advance towards being able to repair biological tissues, e.g. after spinal cord injury. Hydrogels are the key class of materials for soft tissue engineering, but tuning the porosity, cross-linking kinetics, viscoelasticity, and 3D presentation of organized biological cues comes with its own set of challenges when the processes must be compatible with living cells. We developed new enzymatically cross-linked hydrogels providing outstanding possibilities for kinetics, adhesion, and biocompatibility among other interesting properties. We also found that the porosity of synthetic hydrogels can be tuned after injection and in the presence of live cells when making use of a surprising thermodynamic effect, involving dynamically triggered aqueous two-phase systems. Finally, we combined orthogonal enzymatic couplings, photoactivatable ligands, and two-photon-excitation, to pattern growth factors in 3D in complex biological matrices, with micrometer resolution and in the presence of live cells. While we applied these tools successfully to various fields, including cartilage engineering and small intestinal organoid cultures, the expanded toolbox was most notoriously used to solve a variety of neural engineering challenges, including the formation of long-term stable electrically active 3D neural networks in vitro, nerve regeneration through synthetic gels in vivo, and 3D axon guidance using nerve growth factor patterned in a brain-mimetic matrix.

Catalytic Processes for Natural Gas Valorization via Bromine Chemistry

Vladimir Paunović
Advanced Catalysis Engineering, D-CHAB, ETH Zurich

Selective functionalization of methane and other light alkanes into bromoalkanes and their subsequent con-version into value added chemicals and liquid fuels via elimination of hydrogen bromide (HBr) hold a great potential for decentralized valorization of natural gas, which can eradicate the wasting of this abundant re-source by the environmentally harmful flaring practices. The implementation of this technology is contingent on establishing the closed halogen loop, which can be accomplished by the catalytic oxidation of HBr into bromine or catalytic oxybromination of methane with HBr and oxygen to yield bromomethanes. Nonetheless, the corrosiveness of HBr causes a severe deactivation of the oxidation catalysts under preferred low-temperature operation with a stoichiometric feed, while poor catalyst stability and significant losses of bro-minated products via undesired combustion constitute the formidable challenges in oxybromination. By rec-ognizing the resistance to excessive bulk bromination and facile redox cycling as the key descriptors of the supreme HBr-oxidation catalyst, this project led to the identification of europium oxybromide as the first stable active phase enabling to conduct this process in the industrially attractive regime. In addition, fundamental understanding of methane oxybromination was acquired through the synergetic interaction between the materials synthesis and characterization, in-depth kinetic analysis, detection of the gaseous and surface confined intermediates by advanced operando techniques, and density functional theory simulations. This enabled to devise the catalyst design strategies that were verified by a development of vanadyl pyrophos-phate, lanthanum vanadate, europium oxybromide, and supported ceria systems exhibiting unprecedented oxybromination performance. The findings give long-sought momentum to the application of the bromine-mediated natural-gas upgrading.

Additive Manufacturing of Fiber-Reinforced Soft Materials for Medical and Robotic Applications

Manuel Schaffner
Complex Materials, D-MATL, ETH Zurich

Despite the large demand for flexible materials, solely rigid materials such as metals, ceramics and plastics have been accessible to Additive Manufacturing. However, nature unbosoms an entire cosmos of soft materials that transform, morph and even self-heal. Nature uses compliant materials to adapt, interact and conform to its environment – a task that we cannot fulfill with 3D printed parts today. Until now, it was precisely those soft materials that were not accessible to 3D Printing. That is way this thesis focuses on making soft, fiber-reinforced materials accessible to the world of Additive Manufacturing.

Session 3: 15.15 – 16.15

Chair: Prof. Ralph Spolenak (Nanometallurgy, D-MATL)

Cold Sintering – A New Ceramic Processing Route, Investigated Using In-Situ X-Ray Synchrotron Tomography

Matthias Haug[1], Florian Bouville[2], and André R. Studart[1]
[1] Complex Materials, D-MATL, ETH Zurich, [2] Centre for Advanced Structural Ceramics, Imperial College London

One essential step in ceramic processing is sintering. During sintering, a ceramic sample is heated to temperature well above 1'000 °C to remove the porosity, or in other words, to densify the sample. The heating usually takes more than 10 hours and can involve complicated heating profiles to ensure the removal of all additives while not destroying the sample, which makes sintering a time and energy intensive process. In nature, however, ceramic materials can densify under ambient temperature and mild pressure. Inspired from this geological phenomenon, we developed a new ceramic processing route called cold sintering [1]. With the addition of small amounts of water and the application of pressures up to 500 MPa, calcium carbonate nanoparticles can be compacted into structures reaching 85 % relative density within only 30 min. This new process has the potential to reduce the amount of time and energy needed for the sintering process drastically. Unfortunately, at the time being, the process is limited to only a handful of materials and the underlying processes are not yet fully understood. Being able to visualize in situ the process at the length scale of the particles and the correct timescale would provide invaluable information on the exact mechanisms at play. Therefore, we observed the compaction behavior of calcium carbonate particles with X-Ray synchrotron tomography and obtained one 3D volume per minute with a spatial resolution down to 100 nm.

[1] F. Bouville, A.R. Studart, *Nat. Commun*. **8,** 14655 (2017).

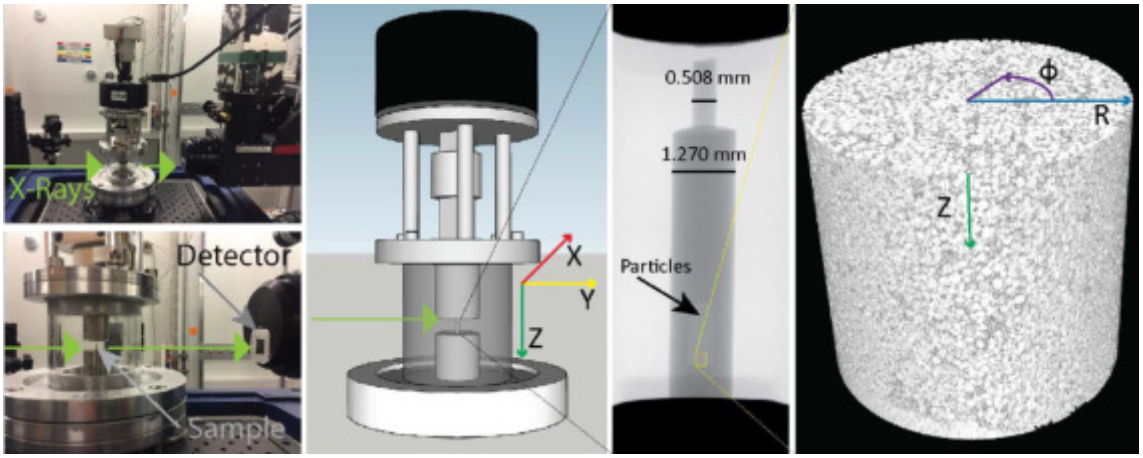


Fig.: Experimental set up for the X-Ray synchrotron tomography. The particles have a diameter of 10 µm.

Nanostructural Properties and Twist Periodicity of Cellulose Nanofibrils with Variable Charge Density

Mario Arcari[1], Elena Zuccarella[1], Robert Axelrod[1], Jozef Adamcik[1], Antoni Sánchez-Ferrer[1], Raffaele Mezzenga[1], and Gustav Nyström[1,2]
[1] Food & Soft Materials, D-HEST, ETH Zurich, [2] WoodTec, Laboratory for Cellulose & Wood Materials, Empa

Cellulose nanofibrils (CNFs) are a renewable and facile to produce nanomaterial that recently gained a lot of attention in soft material research. The nanostructural properties of the fibrils largely determine their self-organizing functionalities, and the ability to tune the CNF nanostructure through control of the processing parameters is therefore crucial for developing new applications. We systematically altered the CNF production parameters (i.e., variation in cellulose source, chemical, and mechanical treatment) to observe their impact on the nanostructural properties of the resulting fibrils. Atomic force microscopy (AFM) allowed detailed topological examination of individual CNFs to elucidate fibril properties such as contour length, kink distribution and the right-handed twist periodicity of individual fibrils. Statistical analysis revealed a large dependency of the fibril properties on the industrial treatment of the cellulose source material. Our results furthermore confirm that the average charge density of the fibrils regulates both contour length and twist periodicity and, thus, has a very strong impact on the final morphology of CNFs. These results provide a route to tune the detailed nanostructure of CNFs with potential impact on the self-organization of these biological colloids and their optimal use in new nanomaterials.

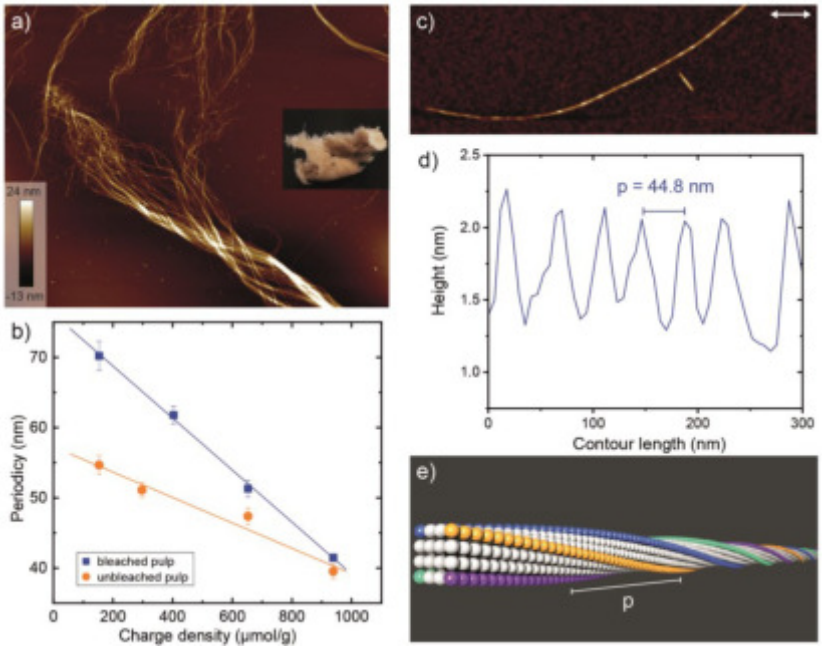


Fig.: (a) AFM image of TEMPO-mediated oxidized softwood pulp. (b) Dependency of periodicity on the charge density of CNFs from bleached (blue square) and unbleached (orange circle) softwood pulp sources. (c) AFM image of a single fibril. (d) Height plot along the contour of a single fibril. (e) Schematic of a twisted 4 × 4-cross section fibril.

Biophysical Regulation of Single Cell Fate in 3D

Oksana Dudaryeva, Marco Lütolf, and Mark Tibbitt
Macromolecular Engineering, D-MAVT, ETH Zurich

Cell function relies on the biophysical and biochemical cues provided by the extracellular microenvironment. These cues include biochemical gradients, niche stiffness, topography and geometry. [1] The individual and synergetic effect of these cues on cell development is still poorly established. The research on this matter is constrained by the limitations of current in vitro cell culture platforms, which offer minimal control over mechanics and the geometrical properties of the individual cellular microenvironments. [2]

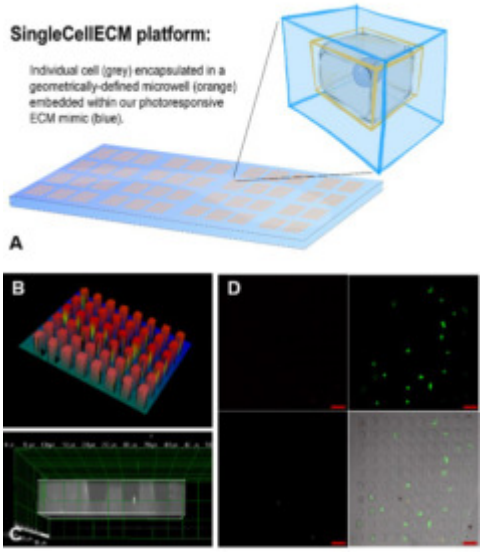


Fig.: (A) Representation of a SingleCellECM platform. (B) White light interferometry image of the micropattern used for the microniche fabrication. (C) Confocal image of microwell structure in hydrogel matrix. (D) Cell viability in large soft niches (125x10^3 µm, 6 kPa) of in vitro cultured hBMSC, represented by live/dead staining. Viable cells are labelled green with Calcein-AM, and dead cells are labelled red with EthD-I, early apoptotic cells are labelled yellow with Annexin V. Scale bars represent 100 µm. Viable cells after 24 h: 79.4 ± 1.8% (n = 2).

To address this challenge, we developed a cell culture platform that offers robust and simultaneous control over niche stiffness, volume, and shape, allowing for decoupling of the different cues that act on the cell. [3] We investigated how increasing niche size and stiffness couple to govern cell viability. The investigation showed that cell exhibit higher viability rates in the microenvironments with higher stiffness and volumes.

[1] V. Vogel, et al., *Nat. Rev. Mol. Cell Biol*. **7**, 265 (2006). [2] M. Tibbitt, et al., *Biotechnol. Bioeng*. **103**, 655 (2009). [3] M. Bao, et al., *Nat. Commun*. **8**, 1962 (2017).

Dynamics of Membrane Wrapping of Microparticles

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[1] Soft & Living Materials, D-MATL, ETH Zurich, [2] Biological Physics, University of Bayreuth

Biological membranes partition eukaryotic cells into different compartments, each of which having its own function and integrity. Moreover, some organelles are characterized by very complex membrane shapes, which seem to confer to them, at least partly, their function. The regulation of biological membrane geometries is therefore crucial.

In vivo, proteins are most probably the main actors of membrane deformation. The underlying physical mechanisms of protein-membrane interactions are not comprehensively understood. 3D membrane geometries can be observed in protein-free systems as well. As the result of the adsorption of particles for example [1,2]. The adsorption of inert particles could thus enable reproduction of the essential physics of membrane deformation by bound proteins. Many numerical and simulation works have predicted how particles behave when adsorbed to membranes [3,4]. However, corresponding experimental data is lacking.

We observe experimentally how micron sized particles bind and subsequently are enveloped by lipid membranes. The lipid membranes are characterized by a bending rigidity κb and a membrane tension σ, which is near zero in our experiments. The polystyrene particles used experience an adhering force introduced by depletion interactions. Both the adhesion energy and particle size can be varied continuously in our system without changing the underlying composition. Due to depletion interactions being used, the experimental system is also independent of the choice of particle material or specific lipid composition of the membrane. We observe the extent of wrapping of the particle over time and see the particle being taken up and effectively recoiling over a distance of one particle radius.

[1] Dietrich, et al., *J. Phys. II* **7**, 1651 (1997). [2] Yu and Granick, *J. Am. Chem. Soc.* **131**, 14158 (2009). [3] Deserno, *Phys. Rev. E* **69**, 031903 (2004). [4] Bahrami, et al., *Adv. Colloid Interfac*. **208**, 214 (2014).

Two-Dimensional Materials as High-Pass Filter of van der Waals Interactions

Tian Tian[1], Franziska Naef[1], Elton Santos[2], and Chih-Jen Shih[1]

[1] Interface & Surface Engineering of Nanomaterials, D-CHAB, ETH Zurich, [2] Computational Materials Design & Theory, Queen's University of Belfast

Understanding and engineering non-covalent van der Waals (vdW) interactions at 2D material interfaces are critical for a large varieties of applications, including molecular epitaxy, self-assembly, wetting properties and vdW heterostructure formation. When two macroscopic bodies are separated by a 2D material, classical pair-wise theory predicts effective penetration of vdW interactions through the few-atom thick 2D layer, leading to phenomena such as wetting transparency. However, such simple picture is challenged by recent experimental advances. Here we present a more precise theoretical analysis, combining modern many-body theory of vdW interactions with fundamental electronic structure of 2D materials, to resolve this controversy. By quantifying the frequency-dependent vdW “transparency”, we show that 2D materials act as high-pass filter of vdW interactions which selectively screen low frequency range interactions (such as Keesom and Debye interactions) due to their highly anisotropic dielectric nature. Such partial transmission of vdW interaction is highly nonlinear, depending primarily on the bandgaps of materials and the spacing between macroscopic bodies. Using the theoretical model, we successfully explain the experimental observation of

screened vdW interaction through 2D materials, which is further endorsed by high level ab initio simulations. Moreover, our model provides an effective approach for high-throughput study on over 105 combinations of bulk and 2D materials, enabling the finding of systems with negative (repulsive) and over-unity (enhanced) vdW transparencies. Our findings reveal the mighty potential of using 2D materials to engineer the interfacial vdW interactions, as well as fundamental insights into the underlying physics.

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ABSTRACTS OF POSTERS

1 Easy and Versatile Enzyme Immobilization on Cellulose Fibers

Christian Goldhahn[1,2], Ingo Burgert[1,2], and Munish Chanana[1,2,3]
[1] Wood Materials Science, D-BAUG, ETH Zurich, [2] WoodTec, Laboratory for Cellulose & Wood Materials, Empa ,[3] Swiss Wood Solutions AG, Zurich

Enzymatic biocatalysis has the potential to enable greener and more efficient synthesis routes for the chemical industry. However, enzymes are often limited to single use applications as they are hard to remove and recover from the reaction solution. As a possible solution for this problem, we developed a robust immobilization of enzymes based on nanoparticle-mediated physisorption on natural macroscopic cellulose fibers. The resulting heterogeneous biocatalyst is easy to handle and can be quickly and completely removed from the reaction solution. The catalytic activity and the multifold reusability of immobilized enzyme are exemplarily investigated for the enzyme laccase. The relative activities of immobilized laccase are evaluated in dependence of pH and temperature and compared to the ones of free enzyme. The potential of multifold reusability of the catalyst is shown for 20 reaction cycles. Furthermore, the application of the approach for the construction of a simple flow-through device is exemplarily shown with the immobilized enzymes glucose oxidase and horseradish peroxidase. The reactor build with the material can execute a two-step reaction cascade.

2 Primary, Secondary, Tertiary and Quaternary Structure Levels in Linear Polysaccharides

Michael Diener, Jozef Adamcik, Antoni Sánchez-Ferrer, Florian Jaedig, and Raffaele Mezzenga
Food & Soft Materials, D-HEST, ETH Zurich

Polysaccharides are ubiquitous in nature and represent an essential class of biopolymers with multiple levels of conformation and structural hierarchy. However, a standardized structural nomenclature, as in the case of proteins, is still lacking due to uncertainty on their hierarchical organization. In this work we use carrageenans as model polysaccharides to demonstrate that several structural levels exist and can be unambiguously resolved by statistical analysis on high resolution AFM images, supported by spectroscopic, X-ray scattering and rheological techniques. In direct analogy with proteins, we identify primary, secondary, tertiary and quaternary structures. The structure–property relationship induced by monovalent ions for κ-, ι- and the non-gelling control λ-carrageenan is established from the single chain regime to the occurrence of hydrogels at higher concentrations. A generality of the observed behavior may be inferred by extending these observations to a distinct class of polysaccharides, the weak carboxylic polyelectrolyte Gellan gum. These results advance our understanding of ion-specific structural changes of polysaccharides and the physical mechanisms responsible for their gelation [1].

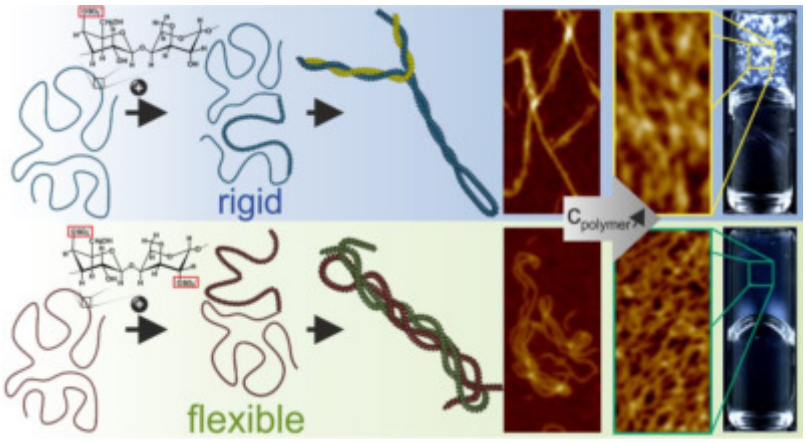

Fig.: Various folding pathways depending on the chain rigidity are followed upon the addition of monovalent ions, resulting in supramolecular assemblies giving rise to self-supporting hydrogels with optical activity. Scale bars represent 100 µm. Viable cells after 24 h: 79.4 ± 1.8% (n = 2).

[1] M. Diener, et al., *Biomacromolecules* **20**, 4 (2019).

3 Linking Kinetics to Viscoelasticity in Dynamic Covalent Hydrogels by 2D 1H NMR

Bruno M. Dufort and Mark W. Tibbitt
Macromolecular Engineering, D-MAVT, ETH Zurich

Dynamic covalent networks form responsive, mouldable, and self-healing materials, as the network cross-links can break and reform in response to external stimuli. The macroscale properties of these networks depend on the specific chemistry of the cross-link binding pairs and the network topology [1]. In this work, boronic ester-based hydrogels (Figure 1a) [2] were used to relate viscoelasticity in model dynamic covalent networks to the microscopic behaviour of the reversible junctions. Oscillatory shear rheometry revealed that tuning network density controlled the plateau modulus G0′ but did not influence the relaxation time τr (Figure 1b), while varying the pH changed τr but did not affect G0′ (Figure 1c). In addition, the kinetics of the boronic ester cross-links obtained using 2D 1H NMR EXSY (Figure 1d) [3] were used to scale the frequency sweeps for gels at different pH (Figure 1e). This work, which links dynamics of the junction chemistry to bulk behaviour, is being used to develop physical models that relate binding pair thermodynamics and kinetics to macroscale properties in order to enable the rational design of dynamic networks.

[1] B. Marco-Dufort and M.W. Tibbitt, *Mater. Today Chem.* **12**, 16 (2019). [2] V. Yesilyurt, et al., *Adv. Mater.* **28**, 86 (2016). [3] J. Lu, et al., *J. Chem. Soc., Dalton Trans.*, 2267 (1998).

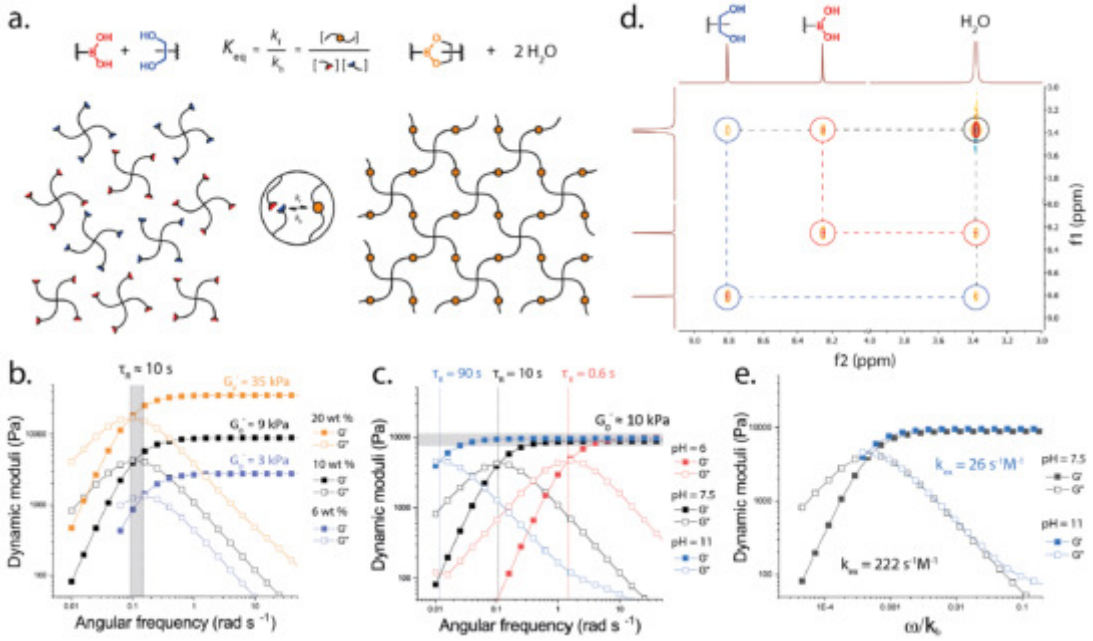

Fig.: a) Reversible network formation for a typical boronic ester-based hydrogel. Frequency sweeps showing plateau modulus G0′ and relaxation time τr are shown for gels formed at b) different weight percentages and c) varying pH. d) A representative 2D 1H NMR spectrum shows how forward and backward reaction rates kf and kb between exchanging boronic acids and diols are obtained in EXSY from the relative intensities of the cross-peaks to the diagonal at different mixing times (0s, 0.3s, and 1.0s). e) Frequency sweeps for gels at different pH scale with the reaction rates obtained from EXSY.

4 Time-Domain Control of Self-Assembly by Means of Complex Chemical Dynamics

Guido Panzarasa and Eric R. Dufresne
Soft & Living Materials, D-MATL, ETH Zurich

Time-domain control for self-assembly by means of chemical programming allows the development of novel biomimetic, adaptive materials.

We provide an account of the results accomplished in our laboratory by coupling different chemical clocks as in situ sources of stimuli (pH, redox) with molecular and macromolecular building blocks to

obtain particles and gels. We show how the formaldehyde-sulfite reaction allows the pH-driven, time-controlled precipitation of chitosan, a biopolymer with broad technological applications [2]. We prove that transient, pH-mediated supramolecular self-assembly of perylenediimide dyes can be achieved with unprecedented temporal control [3]. In addition, we demonstrate how transient complexation-driven self-assembly and supramolecular gel formation can be controlled by means of iodine-based clock reactions [4].

[1] E. Toth-Szeles, et al., *Mol. Syst. Des. Eng.* **2**, 274 (2017). [2] G. Panzarasa, et al., *Soft Matter* **14**, 6415 (2018).

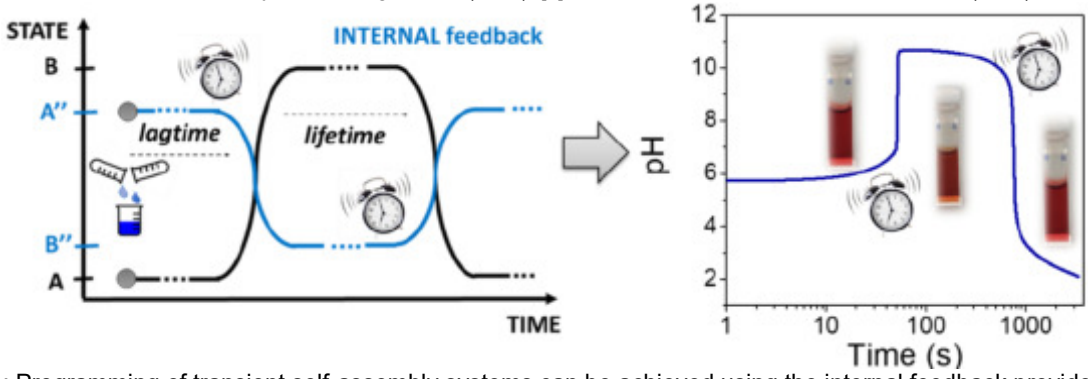

Fig.: Programming of transient self-assembly systems can be achieved using the internal feedback provided by clock reactions.

5 Confinement-Induced Ordering and Self-Folding of Cellulose Nanofibrils

Kathleen B. Smith[1], Jean-Nicolas Tisserant[2,3], Salvatore Assenza[1], Mario Arcari[1], Gustav Nyström[1,4], and Raffaele Mezzenga[1]

[1] Food & Soft Materials, D-HEST, ETH Zurich, [2] Nanotechnology, D-MAVT, ETH Zurich, [3] Institute for High Frequency Technology, Braunschweig University of Technology, [4] WoodTec, Laboratory for Cellulose & Wood Materials, Empa

Cellulose is a pervasive polymer, displaying hierarchical lengthscales and exceptional strength and stiffness. Cellulose's complex organization, however, also hinders the detailed understanding of the assembly, mesoscopic properties, and structure of individual cellulose building blocks. This study combines nanolithography with atomic force microscopy to unveil the properties and structure of single cellulose nanofibrils under weak geometrical confinement. By statistical analysis of the fibril morphology, it emerges that confinement induces both orientational ordering and self-folding of the fibrils. Excluded volume simulations reveal that this effect does not arise from a fibril population bias applied by the confining slit, but rather that the fibril conformation itself changes under confinement, with self-folding favouring fibril's free volume entropy. Moreover, a nonstochastics angular bending probability of the fibril kinks is measured, ruling out alternating amorphous–crystalline regions. These findings push forward the understanding of cellulose nanofibrils and may inspire the design of functional materials based on fibrous templates [1]. [1] K.B. Smith, et. al., *Adv. Sci.* **6**, 1801540 (2019).

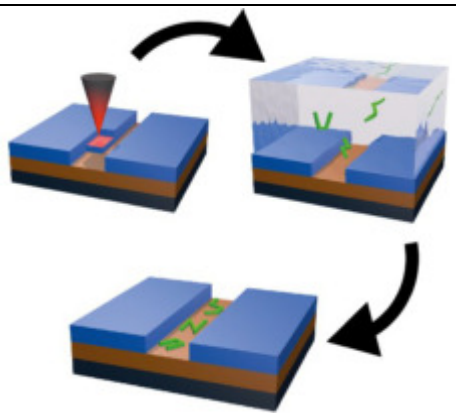

Fig.: Patterning of the substrate by thermal probe lithography. Deposition of the CNFs by adsorption through specific electrostatic interactions. Final sample displaying folded CNFs in a slit of width w and height h.

6 Interaction Between Bacteria and Soft Surfaces Regulated by Surface Physicochemistry or Bacterial Mechanosensing?

Hervé Straub[1,2], Fei Pan[1,3], Claudio M. Bigger[1], Jules Valentin[1], Dominik Abt[4], Xiao-Hua Qin[1], Leo Eberl[2], Katharina Maniura-Weber[1,3], and Qun Ren[1]

[1] Biointerfaces, Empa, [2] Department of Plant and Microbial Biology, University of Zurich, [3] D-HEST, ETH Zurich [4] Department of Urology, Cantonal Hospital St. Gallen

7 Hierarchical Damping of Natural Fibre Composites

Wilhelm Woigk, Kunal Masania, Silvan Gantenbein, Erik Poloni, Alex Heusi, and André R. Studart
Complex Materials, D-MATL, ETH Zurich

8 Development of a Microfluidics-Based Assay in Double Emulsions for the Evolution of Artificial Metalloenzymes

Jaicy Vallapurackal[1], Ariane Stucki[2], Petra S. Dittrich[2], and Thomas R. Ward[1]
[1] Artificial Metalloenzymes, Department of Chemistry, University of Basel, [2] Bioanalytics, D-BSSE, ETH Zurich

9 3D Printing of Fluoride-Eluting Mouthguards

Valentine Berger, Zhi Luo, and Jean-Christophe Leroux
Drug Formulation & Delivery, D-CHAB, ETH Zurich

Sustained drug delivery in the oral cavity remains an important challenge in pharmaceutical science [1]. Currently existing self-application dosage forms are rapidly cleared after administration. The production of oral devices that fit precisely patient's anatomy [2] with local and controlled drug release represents a promising approach to precisely deliver therapeutic compounds to the mouth. In this study, fused deposition modeling (FDM) printer was used to manufacture personalized mouthguards. A single screw extruder was used to produce filaments from an homogeneous mixture of thermoplastics, i.e. poly(L-lactic acid) (PLA), low density poly(ethylene) (LDPE) or linear co-polyester (CoPES, Rowalit®) and sodium fluoride (NaF), a salt commonly used to prevent tooth decay. The composition and thermal properties of the filaments and the printed parts were characterized by thermogravimetric analysis and differential scanning calorimetry. The mechanical properties were assessed for tensile testing and, in vitro dissolution studies were performed.
PLA, LDPE, and CoPES filaments with NaF loadings were produced and successfully printed at 195, 190, and 100 °C, respectively. The filaments tensile stresses at break (70, 12, and 17.5 MPa for PLA, LDPE, and CoPES respectively) indicated that all materials can produce durable devices. In vitro, all filaments prepared with CoPES and LDPE were characterized by a burst of NaF release within the first day. The release rate then leveled off for the CoPES filaments, averaging 0.011 ± 0.002 mg/day for the duration of the experiment (14 days).
Filaments containing NaF have been produced and used for 3D-printing. Further studies will aim at overcoming the problem of high temperature reached during FDM process to introduce temperature sensitive drugs in the mouthguard.
[1] V. Sankar, et al., *Oral Dis*. **17**, 73 (2011). [2] K. Liang K, et al., Sci. Adv. **4**, 1 (2018).

10 A Multiplexed Cell-Free Assay to Screen for Membrane Interacting Peptides in Double Emulsion Droplets

Nicola Nuti, Philipp Rottmann, Ariane Stucki, Sven Krähenbühl, and Petra S. Dittrich
Bioanalytics, D-BSSE, ETH Zurich

11 Microgel Building Blocks for Modular Biomaterial Assembly

Börte Emiroglu[1,2], Bruno M. Dufort[2], Mark W. Tibbitt[2], and Andrew J. deMello[1]
[1] Biochemical Engineering, D-CHAB, ETH Zurich, [2] Macromolecular Engineering, D-MAVT, ETH Zurich

12 Polymeric Materials for 3D Printing of Personalized Biodegradable Airway Stents

Nevena Paunović[1], Yinyin Bao[1], Kunal Masania[2], Nicole Kleger[2], Fergal B. Coulter[2], Annakaroline Geks[3], Karina Klein[3], Peter Kronen[3], Daniel Franzen[4], Brigitte von Rechenberg[3], André R. Studart[2], and Jean-Christophe Leroux[1]
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State-of-the-art airway stents are made of silicone and come in limited number of shapes and sizes. They exhibit a propensity to migrate and are difficult to remove [1]. Here, we report biodegradable polymeric materials for digital light processing (DLP) that would be suitable for the production of personalized airway stents, based on computed tomography (CT) scans of individual patients. A series of reactive copolymers with various molecular weights were synthesized from D,L lactide and ε-caprolactone and used for 3D printing in a customized DLP printer. The materials exhibited highly tunable mechanical properties, depending on the polymer chain length and the feeding ratio of different polymers. The printed stents showed compressive strength comparable to that of a silicone stent, with the additional ability to degrade under physiological conditions. The polymeric materials demonstrated good biocompatibility in preliminary in vitro cytotoxicity tests with HeLa cells. A customized radiopaque CT-based tracheal stent was 3D printed and successfully inserted in the trachea of a rabbit cadaver.

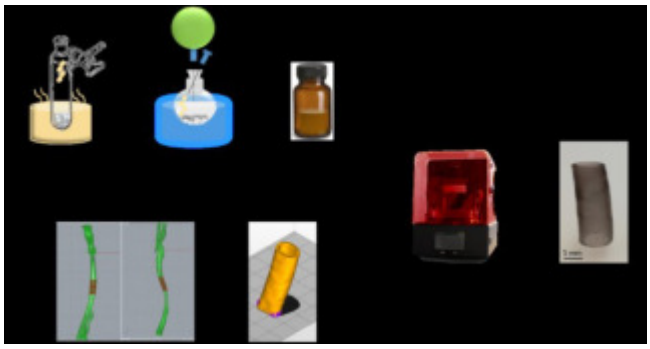

Fig.: Workflow for the production of customized biodegradable airway stents.

Acknowledgement: Financial support from the SNF is acknowledged (Sinergia grant 177178).

[1] A. Ernst and F. J.F. Herth, *Springer,* **ISBN 978-1-4614-4292-9**, 259 (2013).

13 A Facile One-Pot Synthesis of CaO/CuO Hollow Microspheres Featuring Highly Porous Shells for Enhanced CO_2 Capture in Combined Ca-Cu Looping Process via a Template-Free Synthesis Approach

Jian Chen[1,2], Duan Iunbo[2], Felix Donat[1], and Edward J. Anthony[3]

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The preparation of bifunctional CaO/CuO composites with high performance is essential for the development of the combined Ca-Cu looping process, in which the exothermic reduction of CuO with methane is used in-situ to provide the heat required to calcine $CaCO_3$. However, the rapid decline in CO_2 uptake of CaO/CuO composites remains an important problem to be solved, despite their excellent redox characteristic. Herein we report a facile one-pot template-free synthesis approach to yield CaO/CuO hollow microspheres, aimed at enhancing the CO_2 capture performance of CaO/CuO composites. CaO/CuO hollow microspheres feature highly porous shells and a homogeneous elemental distribution, and demonstrate significantly enhanced CO_2 capture performance. After ten repeated cycles in a fixed-bed reactor, CO_2 uptake capacity of the best-performing CaO/CuO hollow microspheres exceeded the reference materials, i.e., CaO/CuO composites synthesized via wet mixing or a co-precipitation method, by 222% and 114%, respectively. Moreover, from cycle number eight onwards, the CO_2 uptake was very stable over the tested 20 cycles, suggesting good cyclic stability of

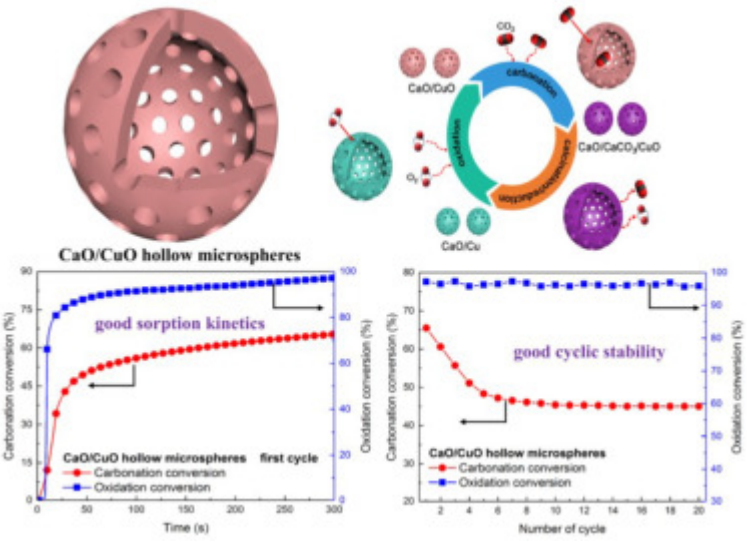

Fig.: Schematic diagram of CaO/CuO hollow microspheres and its cyclic performance.

CaO/CuO hollow microspheres. Oxidation was always fast with conversions greater than 90%. On the basis of N_2 adsorption, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) characterizations, the significantly enhanced CO_2 capture performance of the CaO/CuO hollow microspheres resulted from the unique hollow microsphere structure with highly porous shells, which were retained throughout the cyclic operations.

14 Size Determination of Airborne Graphene Nanoplatelets and Applications in Filtration and Exposure Assessment

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15 Deterministic Nanoprinting of Single Fluorescent Molecules

Claudio U. Hail[1], Christian Höller[1], Korenobu Matsuzaki[2], Patrik Rohner[1], Jan Renger[2], Vahid Sandoghdar[2], Dimos Poulikakos[1], and Hadi Eghlidi[1]
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The controlled integration of single or multiple quantum emitters into a tailored environment is essential to many aspects of quantum photonics and plasmonics. Although various strategies of integration have been pursued, there is still no single best method that fulfills all the requirements for integration. Here, we demonstrate the scalable nanopositioning of single photostable fluorescent molecules with high yield, subwavelength accuracy and well-defined orientation using electrohydrodynamic nanoprinting. We demonstrate the power of our approach by printing arbitrary patterns of molecules and by controllably coupling single molecules to the near field of plasmonic and dielectric optical waveguides [1].
[1] C.U. Hail, et al., *Nat. Commun*. **10**, 1880 (2019).

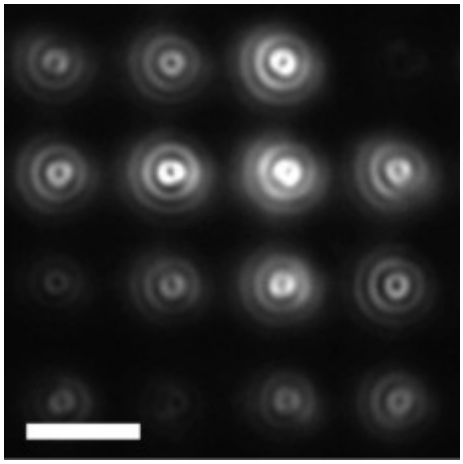

Fig.: A fluorescence image of a nanoprinted square array of terrylene molecules [1]. The scale bar is 2 µm.

16 Characterization of Aerosol Released from the Combustion of Nanoparticle-Containing Materials

Woranan Netkueakul[1,2], Tobias Hammer[1,2], Ari Setyan[1,2], and Jing Wang[1,2]
[1] Chair of Industrial Ecology: Air Quality Control, D-BAUG, ETH Zurich, [2] Advanced Analytical Technologies, Empa

17 Iron Oxide Doped Spray Dried Aluminum Oxide Granules for Selective Laser Sintering and Melting

Stefan Pfeiffer[1,2], Kevin Florio[3], Malgorzata Makowska[4], Dario Ferreira Sanchez[4], Helena Van Swygenhoven[4], Konrad Wegener[3], Christos G. Aneziris[2], and Thomas Graule[1,2]
[1] High Performance Ceramics, Empa, [2] Institute of Ceramic, Glass & Construction Materials, TU Bergakademie Freiberg, [3] Machine Tools & Manufacturing, D-MAVT, ETH Zurich, [4] Photons for Engineering & Manufacturing, PSI

Shaping of complex geometries with high precision and having both high strength and fracture toughness is a key challenge in ceramics processing. This is in combination with long processing time and cost-intensive post processing a major obstacle for a broader application of high tech ceramic parts. Additive manufacturing (AM), especially direct Selective Laser Sintering and Melting (SLS/SLM) could be a solution to these problems.

The absence of understanding the interaction of laser light sources with the ceramics based materials and the slow sintering kinetics of ceramics is today the cause of no existing SLS/SLM process available to consolidate ceramic powders to dense structures. Severe problems like crack formation and weak densification have to be still approached for the production of high performance ceramics with convenient material properties. Powder bed density, flowability, and laser light absorption of the powder strongly influence the processing of the ceramic parts.
Based on our approach the starting ceramic nanosized powders are granulated by spray drying to manufacture highly dense powder with a good flowability. The variation of the composition and morphology of these doped nanocomposite granules affects the absorption behavior to the applied laser light. The focus here is on the optimization of raw powders ratio and additives to improve the interaction between the laser and the granules. It could be shown, that an addition of uniform distributed nano-iron oxide improves the absorption of a green laser light. Final Powders with a tapped density of almost 50% of the theoretical density and an absorbance of 69% (green laser light) lead to densities of laser processed alumina parts of around 96%. [1] The reduction of thermal stresses and cracks formation during laser-processing is also a major challenge to be solved in the ongoing work.
[1] S. Pfeiffer, et al., *Adv. Eng. Mat.,* 1801351 (2019).

18 High-Speed Nanoscale Additive Manufacturing for Dry-Transferred CNT-FET Gas Sensors

Seoho Jung, Cosmin Roman, Miroslav Haluska, and Christofer Hierold
Micro- & Nanosystems, D-MAVT, ETH Zurich

Gas sensors based on dry-transferred, suspended carbon nanotubes (CNTs) show outstanding performance in terms of hysteresis, drift, and power consumption. However, the current fabrication process of these sensors – which involves the fabrication of growth and device substrates, chemical vapor deposition growth of suspended CNTs, optical characterization of CNTs by Raman spectroscopy, and dry transfer of CNTs – is manual, slow, and not scalable for the most parts. Here, a concept for the large-scale production of CNTFET gas sensors, which requires scale-up, batch production, and/or automation of unit processes, is presented. Especially, recent advances in the fabrication of scaled-up substrates and batch-growth of suspended CNTs are highlighted.

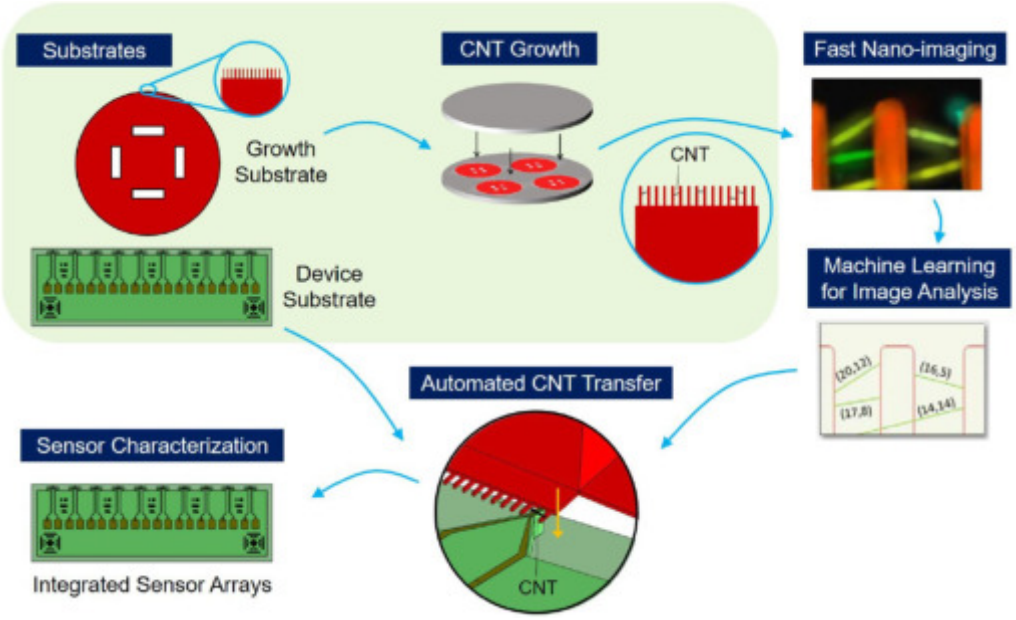

Fig.: Overview of the high-throughput fabrication process of dry-transferred CNTFET gas sensors. This figure highlights activities in the light green box.

19 Model Comparison for Studying Secondary Nucleation by Attrition

Luca Bosetti and Marco Mazzotti
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Secondary nucleation is ubiquitous in nature and of fundamental importance for crystallization processes. Attrition is the mechanism through which fragments form after a collision of a crystal with a stirrer. Those fragments, if small enough, can be considered secondary nuclei.
In this contribution, two population balance equation (PBE) models to simulate secondary nucleation processes have been derived. The traditional approach, developed by Mersmann, describes secondary nucleation as attrition fragments formed through collisions, and their rate of formation is the secondary nucleation rate, which is included in the population balance model as a boundary condition at zero crystal size. In the alternative approach, the formation of attrition fragments is described in the model as a breakage contribution, while the growth rate is accounting for size dependent solubility. Conversely to the traditional model, this formulation takes into account the size distribution of attrition fragments and their evolution due to growth.
In the traditional approach, for the breakage frequency and the attrition daughter distribution, a physical model has been further developed and adapted to PBE. For the secondary nucleation rate, a new expression has been derived and then compared with standard ones.
The two models lead to very similar results, even though they describe the same phenomenon with two fundamentally different approaches. This gives the great flexibility of describing secondary nucleation by attrition as an integro-differential term in the PBE, in the case of breakage, or, alternatively, as a boundary condition, according to the model framework.

[1] S.G. Agrawal and A.H.J. Paterson, *Chem. Eng. Commun*. **202**, 698 (2015). [2] A. Mersmann, Crystallization technology handbook, *CRC Press* (2001). [3] M. Iggland and M. Mazzotti, *Cryst. Growth. Des*. **11**, 4611 (2011).

20 Tip-Enhanced Raman Spectroscopy (TERS) Monitor Selectively Hydrogenation and Hydrogen Diffusion on a Bimetallic Surface

Hao Yin[1,2], Liqing Zheng[1], Wei Fang[1], Jeremy Richardson[1], Yin-hung Lai[1], Bin Ren[2], Jian-feng Li[2], and Renato Zenobi[1]
[1] Organic Chemistry, D-CHAB, ETH Zurich, [2] Xiamen University, China

Catalytic hydrogenation has diverse important industrial uses. Most frequently, industrial hydrogenation relies on heterogeneous catalysts especially novel metal hydrogenation catalysts such as palladium (Pd), platinum (Pt). While a single metal catalyst is not enough to achieve both high efficiency and selectivity, researchers have developed several bimetal catalyst with different structures including core-shell, alloy and Janus structures. Therefore, it is important to directly reveal the reactive site in bimetal system. Tip-enhanced Raman spectroscopy (TERS) combines plasmon-enhanced Raman spectroscopy with scanning probe microscopy to simultaneously provide chemical fingerprint and morphological information of samples with nanometer spatial resolution. TERS is an ideal tool for achieving an in-depth understanding of surface and interfacial processes, so that a relationship between structure and chemical performance can be established [1].

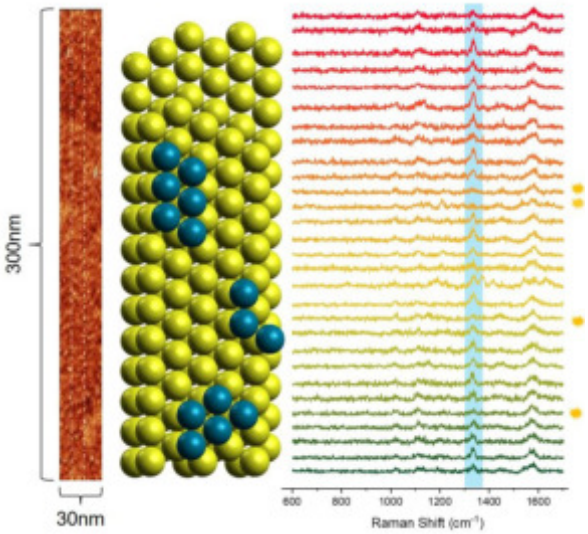

Fig.: STM image (left) and corresponding TERS mapping of certain line-scan (right).

In this work, we utilized TERS with 10nm/pixel spatial resolution to reveal the performance of a bimetallic (Pd/Au) model catalyst. By using under-potential deposition [2], we created a submonolayer of Pd on Au(111). We can clearly identify where the hydrogenation reaction happens by

matching TERS maps with STM images. Similar to result from industrial catalysis research, we confirm that the hydrogenation reaction mainly happens on Pd rather than on Au, mainly as a result of the different hydrogen dissociation ability.

[1] X. Wang, et al., *Chem. Soc. Rev*. **46**, 4020 (2017). [2] J. Zhong, et al., *Nature Nanotech*. **12**, 132 (2017).

21 Studying Nickel Distribution in $LiNi_xMn_yCo_zO_2$ (NMC) Cathode Materials

Nils Wenzler[1], Ramesh Shunmugasundaram[1], Vincent De Andrade[2], Francesco De Carlo[2], and Vanessa Wood[1]

[1] Materials & Device Engineering, D-ITET, ETH Zurich, [2] Imaging Group (IMG), X-ray Science Division (XSD), Argonne National Laboratory Lemont

$LiNi_xMn_yCo_zO_2$ (NMC) cathode materials with a high nickel content (x=0.6 to x=0.8) are excellent candidates for high energy density Li-ion batteries. However, after prolonged cycling of these NMC compounds, fracturing of the active particles is often observed [1]. Using large-area X-ray energy dispersive spectroscopy (XEDS), Gu et al. showed that Ni ions segregate. This leads to uneven Ni distribution in nanoscale primary particles [2]. It is important to understand the distribution, and possible redistribution upon cycling, of Ni and the influence it has on morphological changes in the particles.

Here, we examine imaging techniques that can be used to quantify Ni distribution, redistribution upon cycling and fracturing in NMC materials. We show the potential benefits of two-energy X-ray tomographic microscopy to obtain a map of the Ni-content as well as an accurate reconstruction of the particle on samples.

We cycled three different commercially available NMC compounds (NMC532, NMC622, and NMC811). Pristine and cycled electrodes were embedded with epoxy resin and laser milled to 70 m diameter cylinders needed for high resolution imaging at the transmission x-ray microscope (TXM) at the Advanced Photon Source (APS). By acquiring two tomograms of each sample at different energies, one above and one below the Ni k-edge, we can isolate the absorption coming from the Ni-phase. This allows us to simultaneously map in 3D the Ni concentration and structure of a number of particles in the electrode samples.

[1] A.O. Kondrakov, et al., *J. Phys. Chem.* **121**, 3286 (2017). [2] M. Gu, et al., *Nano Lett.* **12**, 5186 (2012).

22 Modelling of a Thermochemical Storage Reactor

Michael Wild and Aldo Steinfeld

Renewable Energy Carriers, D-MAVT, ETH Zurich

Concentrated Solar Power (CSP) systems make use of solar energy as the source of high-temperature process heat to provide renewable energy at competitive prices. One major drawback of solar radiation is its intermittency due to day/night cycles, weather and seasons. Thus, effective use of CSP technology requires the ability to store thermal energy and release it once it is needed. Thermal energy storage (TES) directly stores solar heat and therefore avoids inefficient transformations into other forms of energy. In addition, TES makes use of abundant, inexpensive materials. Three forms of TES are generally considered: sensible, latent and thermochemical. Sensible heat storage utilizes the heat capacity of the storage material, while latent storage utilizes the energy needed to drive a phase change in a material. Thermochemical storage stores energy in the reaction enthalpy of reversible endothermic/exothermic chemical reactions such as the calcination/carbonation of limestone. By influencing the reactant gas partial pressure inside the thermochemical storage reactor, the reaction rate and thus energy release/uptake can be controlled. A combined storage consisting of a sensible heat section with a packed-bed of rocks and a thermochemical section on top with a chemical reactor further provides controllability of the heat transfer fluid outflow temperature. This in turn is crucial for the operation of the power block downstream and a deciding factor when assessing the power plant performance. The reactants are stored separately, providing lossless longterm storage. A detailed heat and mass transfer model of the thermochemical section has been developed for guiding the design, material choices, and optimization, as well as for the identification of limiting effects and adequate control strategies. The model will be experimentally validated with data obtained with a lab-scale reactor prototype using a reversible carbonation/calcination gas-solid reaction.

23 Imaging of Ceramic Coated Lithium Ion Battery Separators

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Materials & Device Engineering, D-ITET, ETH Zurich

Separators in Lithium Ion Batteries (LIBs) are electronically isolating membranes that prevent physical contact between the two electrodes while allowing ionic transport. Therefore, they are considered to be all crucial part in battery safety.
In commercially available LIB, separators are predominately made from porous polyolefin films such as polypropylene (PP) or polyethylene (PE). Separators can also be coated with thin layers of ceramics (e.g., Al_2O_3, MgO_2, …) which improves their wettability (facilitating manufacturing and lithium ion transport), stability against shrinking in response to thermal stress or under shutdown conditions, and their resistance to electrochemical oxidation from a high voltage positive electrode.
Traditional parameters for the characterization of LIB separators include the effective transport coefficient (ratio between porosity and tortuosity). However, to fully capture all aspects of battery performance, additional parameters like pore space connectivity are necessary [1,2].
Our research group developed an approach to visualize and quantify the polyolefin separators with focused ion beam scanning electron microscopy (FIB-SEM) [3]. By comparing the 3D tomographic data of coated and uncoated PE separators, we can quantify the influence of the ceramic coating on performance and structure.
[1] M. F. Lagadec, et al., *Energy Environ. Sci.* **11**, 3194 (2018). [2] M. F. Lagadec, et al., *Nat. Energy* **4**, 16 (2019). [3] M. F. Lagadec, et al., *J. Electrochem. Soc.* **163**, A992 (2016).

24 Growth Optimization of Electrodeposited Bismuth Selenide for Thermoelectric Application

Katrina Klösel, Ian A. Mihailovic, and Christofer Hierold
Micro- & Nanosystems, D-MAVT, ETH Zurich

Electrodeposition is a common film deposition method and is advantageous due to its simplicity and low cost [1]. However the film growth strongly depends on the deposition parameters which need optimization for every new material combination. Bismuth selenide is a promising material for memristive [2,3] and thermoelectric [4,5] applications. This poster presents preliminary results of material growth, morphology and composition of electrodeposited bismuth selenide into SU-8 templates of tens of microns thickness utilizing an optimized set of parameters. An outlook on how to further optimize the deposition parameters for improved thermoelectric performance, in particular in view of n- and p-type behavior, and how to measure relevant parameters such as thermal and electrical conductivity and Seebeck coefficient is given.
[1] C. Boulanger, *J. Electron. Mater.* **39**, 9 (2010). [2] X. Zhang, et al., *Appl. Phys. Lett.* **107**, 10 (2015). [3] N. A. Tulina, et al., *Bull. Russ. Acad. Sci. Phys.* **80**, 6 (2016). [4] Z. Sun, et al., *Dalton Trans.* **39**, 10883 (2010). [5] Kulsi et al., *Curr. Appl. Phys.* **17**, 1609 (2017).

25 Transparent and Flexible Thin-Film Supercapacitor/Hybrid-Supercapacitor Based on Porous Carbon with High Capacity

Tian Liu[1], Runyu Yan[2], Long Pan[1], and Markus Niederberger[1]
[1] Multifunctional Materials, D-MATL, ETH Zurich, [2] Max Planck Institute of Colloids and Interfaces Potsdam

Transparent and flexible energy storage devices have received immense attention due to their unique optical and mechanical qualities for innovative wearable electronics. However, it still remains a great challenge to fabricate devices with high capacities and high degree of transmittance, especially by using a universal fabrication process for both supercapacitor and hybrid-supercapacitor. Here, we use a method for fabricating transparent and flexible thin-film supercapacitor/ hybrid-supercapacitor with high transparency and capacity. The fabricated transparent and flexible supercapacitor exhibits area capacitance of 1072 $\mu F/cm^2$ at the current density of $30\mu A/cm^2$ and high transparency of 71.8%. We also demonstrated that by using the same process the transparent and flexible hybrid-supercapacitor displays high transparency of 72.4% and 1302.5 $\mu F/cm^2$ of area capacitance at the current density of $30\mu A/cm^2$, significantly higher than the reported electrodes with comparable transparency.

With bending of 45°, the supercapacitor and hybrid-supercapacitor still have 93.1% and 90.3% capacity retentions even after cycling over 1000 times. These findings opens up new ways to use various electrode materials and universal methods for flexible and transparent supercapacitors/hybrid-supercapacitors.

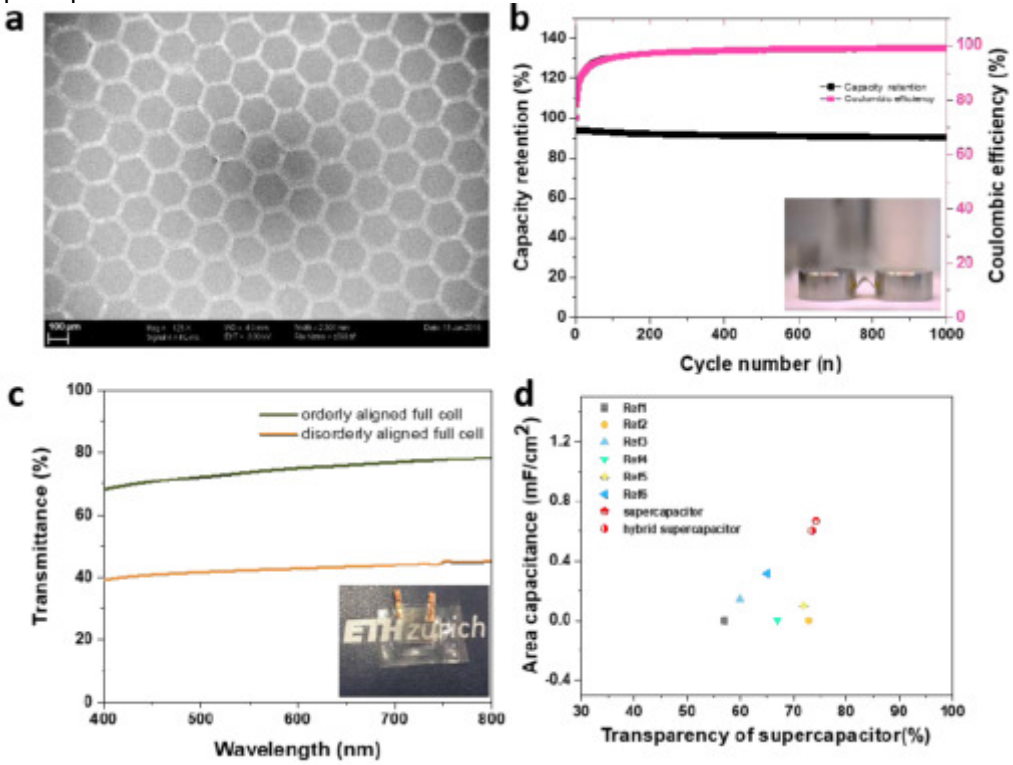

Fig.: (a) SEM picture of Ag nanoparticles + porous carbon electrode. (b) Capacity retention and coulombic efficiency of transparent and flexible thin-film supercapacitor. Inset: optical image of supercapacitor with 45° bending. (c) Transmittance of orderly and disorderly aligned supercapacitor. Inset: optical image of transparent and flexible supercapacitor. (d) Comparisons of transparency and area capacitance between references and fabricated supercpacitor/hybrid-supercapacitor.

26 Signatures of Temporary Carrier Trapping in Single CdSe/CdS Core/Shell Quantum Dots

Sander J.W. Vonk[1], Stijn O.M. Hinterding[2], Elleke V.H van Harten[2], and Freddy T. Rabouw[2]
[1] Optical Materials Engineering, D-MAVT, ETH Zurich, [2] Soft Condensed Matter, University Utrecht

27 Gain Mediated Surface Plasmon Polariton Propagation in the Near-Infrared

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[1] Nano-Device Physics, D-ITET, ETH Zurich, [2] Materials Integration & Nanoscale Devices (MIND), IBM Research Zurich, [3] Institute of Electromagnetic Fields, D-ITET, ETH Zurich, [4] Institute of Advanced Optics & Photonics, Hanbat National University Daejeon

We demonstrate gain mediated propagation of hybrid plasmonic-photonic modes in the near-infrared (NIR) at temperatures ranging from 95K to 300 K. Hybrid modes are formed in a thin oxide layer sandwiched between a gold (Au) film and an indium phosphide (InP) substrate. Optical pumping at 750 nm results in photoluminescence (PL) from InP which couples to surface plasmon polaritons. In contrast to the PL efficiency, the plasmonic propagation losses are quasi temperature independent. We attribute this weak dependence predominantly to scattering caused by the Au film's polycrystallinity [1].

[1] S.V. Jayanti, et al., *Opt. Mater. Express* **5**, 1147 (2015).

28 Direct Single-Shot Measurement of Orbital Angular Momentum from Colloidal-Quantum-Dot Ring Lasers

Robert C. Keitel, Boris le Feber, Krispin Dettlaff, Eva De Leo, Maria del Henar Rojo Sanz, and David J. Norris
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Orbital angular momentum (OAM) is a degree of freedom of light that can be used to encode information in optical communication or for advanced nanoparticle-trapping applications. While conventionally OAM is imprinted on a laser beam using bulky far-field optics, miniaturization requires more compact and integrated sources of OAM. Our lab has recently developed a template-stripping technique for the fabrication of high-quality quantum-dot ring lasers with quality factors up to ~2500 under pulsed excitation. Integrating a grating within these rings allows diffraction of the lasing mode into a spatially coherent OAM-carrying beam where the topological charge can be tuned via the grating pitch. By using a cylindrical lens in combination with careful spatial filtering, we transform the far-field pattern, which features complex intensity, phase, and polarization distributions, into an image from which we directly extract the topological charge. In a typical measurement, where the signal is integrated over 100s to 1000s of laser shots, we observe symmetric patterns, indicating the presence of an OAM with positive and negative sign. We attribute this finding to the presence of clockwise- and counter-clockwise propagating modes each giving rise to one handedness of OAM. Following this hypothesis, we further demonstrate that, when isolating one circularly polarized component of the laser emission, a non-symmetric pattern linked to an OAM state of pure handedness is observed. This suggests that the direction of propagation of the active mode has a direct impact on the handedness of both the circular polarization and the topological charge of the emitted beam. Finally, we statistically analyze sequences of individual laser shots and find that degenerate modes of opposite handedness are anticorrelated, suggesting that this ring-laser system is governed by pairs of competing modes at each resonance and not by a coupled mode as it was observed in other types of ring resonators.

29 Lithium Niobate as a Platform for Integrated Photonic Devices with Complex Geometry

Sissi Wang[1], Marc Reig Escalé[1], Fabian Kaufmann[1], David Pohl[1], Michele Gaio[2], Stefano Vezzoli[2], Dhruv Saxena[2], Romolo Savo[1], Riccardo Sapienza[2], and Rachel Grange[1]
[1] Optical Nanomaterials, D-PHYS, ETH Zurich, [2] Complex Nanophotonics, Department of Physics, Imperial College London

This project aims to explore classical and quantum light propagation in disordered nanoscale waveguide networks as a novel route to scalable optical and quantum information processing.
This is motivated by research in several different fields. Photonic networks have been studied as a communication platform, in which information is transmitted as optical signal. Besides using photons to increase the quantity of transported signals compared to electrons, it is now established that the introduction of some disorder within the network, i.e. random position of the channels cross-links, can increase the amount of transmitted data. On the other hand, quantum random walks have been shown to have high computational complexity, even in a passive and linear optical system (Boson sampling). Therefore we aim to utilise complex network geometries and multiple scattering phenomena of light to build an information processing platform more scalable and robust than circuit-based optical quantum computing platforms.
We will first describe fabrication results achieved using the integrated lithium niobate ($LiNbO_3$) platform. In particular, we demonstrate tunable refractive index in the material achieved using electro-optic effect [1]. We will further introduce a simple waves-on-graph model that enables efficient simulation and modelling of light scattering and transport in large complex networks [2]. Relation to multiple scattering and localisation effects in disordered media is also briefly discussed.
[1] M. Reig Escalé, et al., *Opt. Lett.* **43**, 1515 (2018). [2] M. Gaio, et al., *Nat. Commun.* **10**, 26 (2019).

30 Low-Temperature Drexhage Experiments on Colloidal Semiconductor Nanocrystals

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In typical time-resolved photoluminescence (TRPL) measurements of fluorescent emitters, complex and multi-component decay dynamics are often observed and the interpretation of those can sometimes be puzzling. One way to shine more light is modify the electromagnetic environment by careful control of the local density of states (LDOS) of the surroundings of the emitter. Pioneering experiments were made by Drexhage [1], who first showed that the lifetime of emitters can be modified by controlling the LDOS. This method allows, in principle, to experimentally determine the radiative and nonradiative recombination rates of the excited state [2].

We perform similar experiments to Drexhage and extend them to colloidal semiconductor nanocrystals down to cryogenic temperatures, where the effects of band-edge exciton fine structures [3] in photoluminescence decays are more prominent. This is experimentally realized by simply placing colloidal emitters close to a metallic mirror, separated from it by a dielectric layer with a controlled thickness gradient, and recording their fluorescence lifetimes at various temperatures. The experiments therefore provide a further insight into band-edge exciton fine structures, besides a temperature dependent quantum yield.

[1] K.H. Drexhage, *J. Lumin.* **1/2**, 693 (1970). [2] X. Brokmann, et al., *Phys. Rev. Lett.* **93**, 107403 (2004). [3] M. Nirmal, et al., *Phys. Rev. Lett.* **75**, 3728 (1995).

31 Nondestructive Microstructure and Mechanical Characterization Through Optical Probing

Joan Sendra Garcia and Ralph Spolenak
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Nondestructive mechanical characterization of materials is usually carried out by Raman spectroscopy or X-ray diffraction. However, both Raman spectroscopy and labscale XRD do not work on metal thin films due to their polarizability and low interaction volume, respectively. In contrast, reflectance anisotropy spectroscopy (RAS), an optical technique where the difference in reflectance between orthogonal polarizations under near normal incidence is measured, can be used for mechanical characterization of thin films [1]. Here we suggest a novel approach to use RAS for both mechanical and microstructure in situ studies of thin films. Since RAS is sensitive to out of plane crystal orientation, specifically under tensile stress [2], and azimuth dependent RAS (ADRAS) is sensitive to in-plane crystal orientation [3], we propose to combine RAS microscopy together with ADRAS to map the grain crystal orientation and strain distribution in polycrystalline materials, in a similar fashion to electron backscatter diffraction (EBSD).

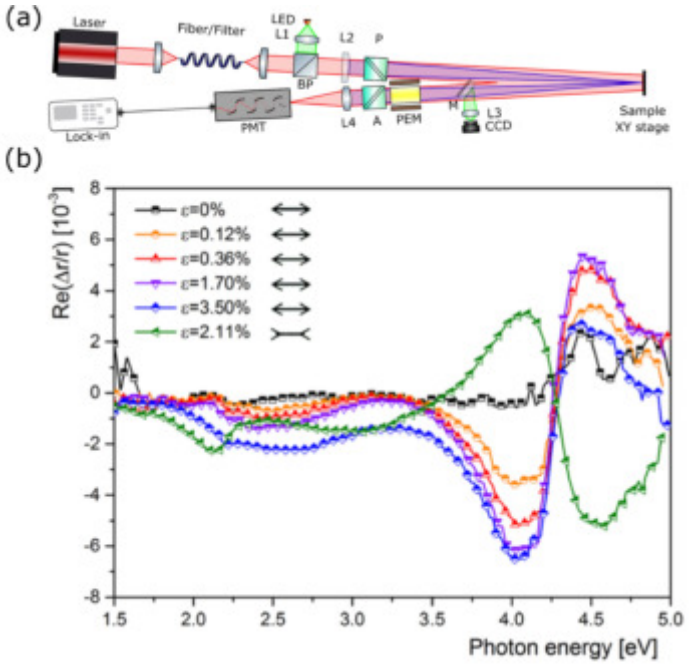

Fig.: (a) Schematic of the RAS microscopy setup. (b) Mechanical characterization of polycrystalline copper thin films [1].

[1] A. Wyss, et al., *J. Phys. D Appl. Phys.* **48**, 415303 (2015). [2] D. Papadimitriou and W. Richter, *Phys. Rev. B* **72**, 075212 (2005). [3] J. Tao, et al., *ACS nano* **9**, 11362 (2015).

32 Under Pressure: Solids Growth in an Elastic Network

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Nature assembles structures with exceptional properties providing extraordinary control over their composition and size. Nacre, for example, uses common compounds like brittle calcium carbonate as basis for an incredibly tough biocomposite [1]. Structural colours are another example. Living organisms often display very bright, non-fading colours thanks to confined biological nanostructures able to interact with specific wavelengths of light [2].
In all these cases, solids self-assemble in materials with controlled shape, size, orientation and spatial distribution.

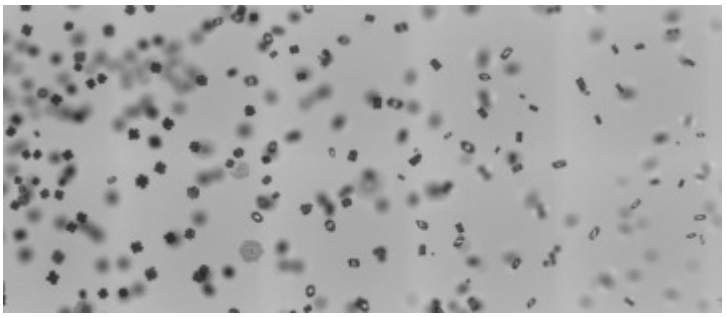

Fig.: Calcite crystals gron in poly(ethylene glycol) diacrylate.

To achieve the same goal, we use polymeric networks to template and control the growht of crystals and other synthetic materials. In particular, we study how the properties of the elastic matrix affect the solids growth and we use these concepts to design new materials.

[1] F. Barthelat, et al., *J. Mech. Phys. Solids* **55**, 2 (2007). [2] E. Dufresne, et al., Soft Matter **5**, 1792 (2009).

33 Towards Mapping Wear Performance

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34 Stiff Composite Cylinders for Extremely Expandable Structures

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The realization of concurrently largely expandable and selectively rigid structures poses a fundamental challenge in modern engineering and materials research. Radially expanding structures in particular are known to require a high degree of deformability to achieve considerable dimension change, which restrains achievable stiffness in the direction of expanding motion. Mechanically hinged or plastically deformable wire-mesh structures and pressurized soft materials are known to achieve large expansion ratios, however often lack stiffness and require complex actuation.
Cardiovascular or drug delivery implants are one example which can benefit from a largely expandable architecture that is simple in geometry and intrinsically stiff. A possible solution pose continuous shell cylinders. However, no designs exist that achieve large expansion ratios in such shells when utilizing materials which can provide considerable stiffness.
We introduce a new design paradigm for expanding continuous shells that overcomes intrinsic limitations such as poor deformability, insufficient stiffness and brittle behavior by exploiting purely elastic deformation for self-expandable and ultra-thin polymer composite cylinders. By utilizing shell-foldability coupled with exploitation of elastic instabilities, we create continuous cylinders that can change their diameter by more than 2.5 times, which are stiff enough to stretch a confining vessel with their elastic energy. Based on folding experiments, finite element simulation and analytical models, we predict feasible radial expansion ratios currently unmatched by comparable cylindrical structures.
To emphasize the potential as a future concept for novel simple and durable expanding implants, we demonstrate the functionality on a to-scale prototype in packaging and expansion and predict feasible constellations of deployment environments.

35 Helium Ion Irradiation of Single Crystal Diamond: Orientation-Dependent Structural Damage and Resulting Micro-Mechanical Response

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Microfabrication of synthetic single-crystal (SC) diamond using accelerated helium ion beam has significant potential in high-precision optical devices, through tailoring optical properties via diamond graphitization. In principle, the use of helium ion microscopes (HIMs) with nano-scaled focused ion beam spot size will allow for precision nano-patterning of the diamond surface through post-exposure selective etching of generated graphitic phase. Here, SC diamond with <100>-, <110>-, <111>- and <123>-presenting crystalline orientations were exposed to He-ion radiation using a HIM, at a range of dose and acceleration voltages. The damaged structure was investigated using confocal Raman spectroscopy and scanning electron microscopy (SEM), and it was observed that <100> and <110> orientation were significantly less sensitive to <111> and <123>. This effect was further studied using in situ uniaxial compression of as-fabricated and irradiated <100>- and <123>-oriented micro-pillars (shown in Figure 1). The results show that irradiation damage of energetic helium ions on the structure and mechanical properties of diamond is therefore highly orientation-dependent, and may be widespread in anisotropic crystals. Such results afford critical knowledge of ion damage for precise HIM nanofabrication, with implications for nuclear applications. that cell exhibit higher viability rates in the microenvironments with higher stiffness and volumes.

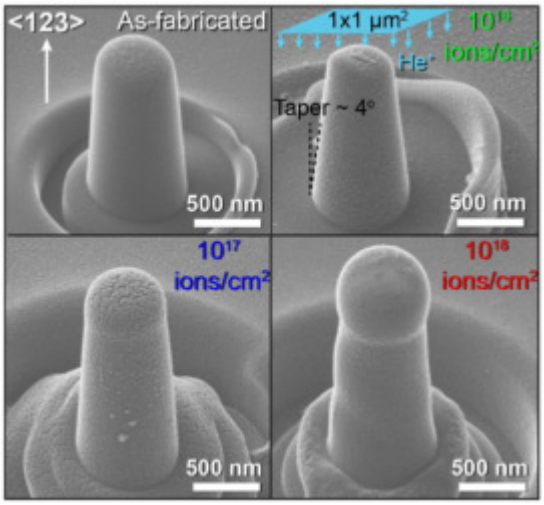

Fig.: Helium ion microscope of diamond pillars irradiated with varying helium doses under 30 keV acceleration.

36 Strain-Controlled Dimensionality of Interface Metallicity in $LaVO_3/LaTiO_3$ Multilayers

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Complex oxide thin films and heterostructures exhibit a wide variety of interesting functionalities that emerge at their interfaces, which are often not present in the corresponding bulk components. Due to the strongly correlated electrons in early transition metal oxides, these materials are at the border between localized and itinerant behaviour and thus, remain challenging to describe in electronic structure calculations. Here, we report on a metallic interface in multilayers of two Mott insulators, $LaVO_3$ and $LaTiO_3$, using a combination of density functional theory (DFT) and dynamical mean-field theory (DMFT) [1]. We show that the metallic layer results from charge transfer across the interface, which alters the valence state of the transition metal cations close to the interface. Somewhat counter-intuitively, the direction of the charge transfer increases the occupation difference of the t2g states, which can be understood as a result of a gradual transition of the charge transfer energy, or electronegativity, across the interface. We demonstrate that the spatial extension of the metallic layer, in particular towards the $LaTiO_3$ side, can be controlled via epitaxial strain, with tensile strain leading to a localization within a thickness of only two unit cells.

[1] S. Beck and C. Ederer, *arXiv*:1905.00290 (2019).

37 Functional Materials Made From Upscaled Microfluidic Processes

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38 The "Quenching Problem" in Intrinsic Heat Source Healing of Metal Thin Films

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39 Three-Dimensional Printing of Hierarchical Liquid Crystal Polymer Structures

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Fibre-reinforced polymer composites are often used when stiff and strong materials are required for lightweight applications. However, these materials require energy- and labour-intensive fabrication processes, exhibit typically brittle fracture and are difficult to shape and recycle. This is in stark contrast to biological lightweight materials such as bone, silk and wood, which demonstrate complex hierarchically structured shapes with outstanding mechanical properties by utilising directed self-assembly to grow structures. Here, we demonstrate a bioinspired 3D printing approach to create lightweight structures with hierarchical architectures, complex geometries and unprecedented stiffness and toughness. Their features arise from the self-assembly of liquid crystal polymer molecules into highly oriented domains during extrusion of the molten feedstock material using the widely accessible fused deposition modelling approach. By orienting the molecular domains with the print path, we can reinforce the polymer according to the predicted mechanical stresses. The resulting material is recyclable and exhibit stiffness, strength and toughness that outperform state-of-the-art 3D printed polymers by an order of magnitude and rivals even the highest performance lightweight carbon fibre-reinforced composites.

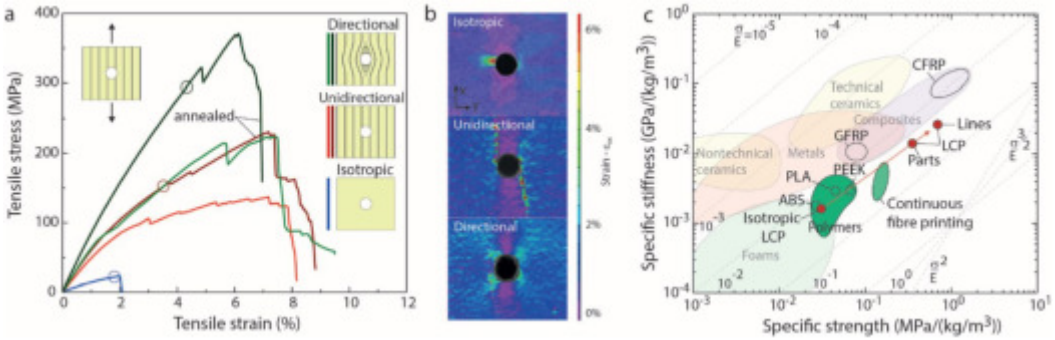

Fig.: a) Stress-strain curves of OHT samples with different print architectures (annealed and unannealed), b) DIC stress maps corresponding to the circles in a, c) Ashby diagram showing the specific stiffness and strength of typical engineering and 3D printing materials compared to the mechanical properties of the LCP material printed in this study.

40 Direct Observation of Electron Density Reconstruction at the Metal-Insulator Transition in $NaOsO_3$

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The metal-insulator transition in 5d transition metal oxide $NaOsO_3$ which occurs concomitantly with antiferromagnetic transition (T_{MIT}=T_N) has been proposed to be of Slater mechanism [1,2] i.e. it is the onset of the antiferromagnetic order that drives the system into an insulating state [3]. However, there is no consensus and other mechanisms such as a Lifshitz transition have also been proposed [4]. We employed static non-resonant and resonant x-ray single crystal diffraction at the Os L_2,3 edges in order to obtain details of the Os electron density deformation across T_{MIT} and to determine the microscopic mechanism of the phase transition. In case of a Slater metal-insulator transition, there should be no change in the crystallographic symmetry and, indeed, our off-resonance single crystal x-ray diffraction experiments find no evidence of crystallographic symmetry breaking across the metal-insulator transition. In addition, using an incident x-ray energy corresponding to the Os L_3 resonant edge, we observe the emergence of a diffracted intensity at the (300) forbidden reflection at T_{MIT}=T_N for a specific energy E_A = 10.878 keV. The intensity of this space-group forbidden peak increases continuously with decreasing temperature and is not of magnetic origin. Rather, we show that it is due to a change in the Os electron density associated to the onset of long range antiferromagnetic ordering (see Fig.). Thus, the main conclusions of our experimental results, namely the absence of crystallographic symmetry breaking and the presence of antiferromagnetic driven Osmium electron density reconstruction, support the first realization of a Slater insulator, $NaOsO_3$ [5].

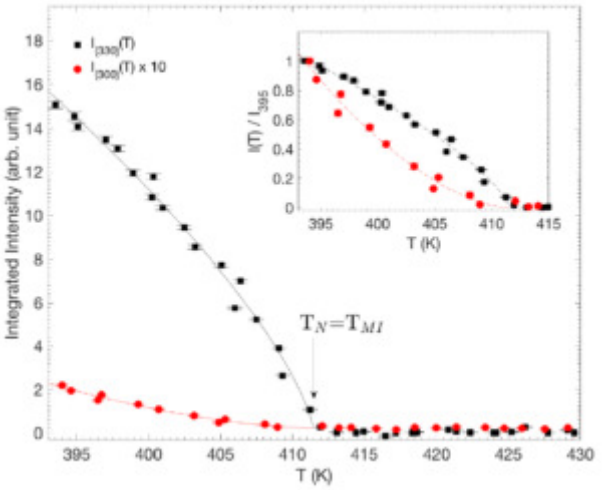

Fig.: Comparison of temperature dependent intensity of (300) forbidden and (330) magnetic reflections at an x-ray photon energy corresponding to E_A = 10.878 keV. In the inset, the same data in the vicinity of T_N and normalized by the intensities of the respective reflections measured at T = 395 K are shown.

[1] J.C. Slater, *Phys. Rev.* **82**, 538 (1951). [2] Y.G. Shi, et al., *Phys. Rev. B* **80**, 161104 (2009). [3] S. Calder, et al., *Phys. Rev. Lett.* **108**, 257209 (2012). [4] B. Kim, et al., *Phys. Rev. B* **94**, 241113 (2016). [5] N. Gurung, et al., *Phys. Rev. B* **98**, 115116 (2018)

41 Numerical Analysis of the Acoustic Radiation Force on an Elastic Sphere in a Viscous Fluid Including Acoustic Streaming

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The force driving the motion of a particle suspended in a fluid in an acoustic field is called the acoustic radiation force (ARF). This concept is, for example, commonly applied in lab-on-a-chip devices for manipulation of cells and other objects [1].
In this numerical study, we investigate the ARF acting on an elastic spherical particle submerged in a viscous fluid in an ultrasonic acoustic field. We used the finite-element method COMSOL Multiphysics software framework to formulate

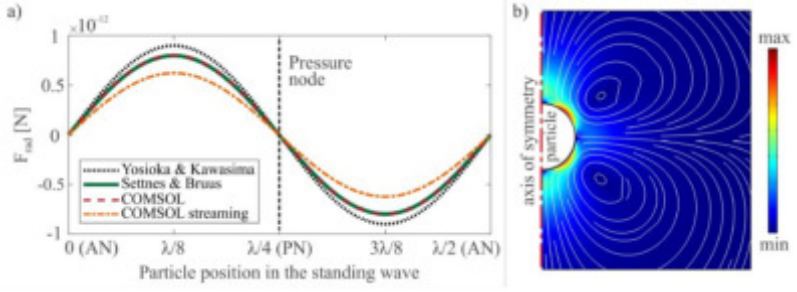

Fig.: a) The acoustic radiation force along the direction of wave propagation, acting on a polystyrene sphere with radius of a = 10 μm, submerged in oil with one-dimensional background standing wave with frequency of 0.05 MHz. COMSOL: numerical results without streaming; COMSOL streaming: numerical results with streaming. b) The acoustic streaming flow field around the particle placed at the pressure node (PN). Red and blue colors indicate high and low velocity amplitudes, respectively. The streamlines are shown in white.

the numerical models used in the study. In contrast to the existing numerical studies [2], we consider viscous effects including the contribution of the acoustic streaming. In the process, we numerically solve the sets of viscous first- and second-order equations following from the perturbation theory. The equations are explicitly solved outside and inside the viscous boundary layer. We compare our numerical results to analytical models, such as the non-viscous model by Yosioka and Kawasima [3] and the viscous model by Settnes and Bruus [4]. Our model shows that the acoustic streaming around the particle in a one-dimensional plane standing wave can greatly influence the ARF. For example, we observed a decrease in the ARF for a solid elastic particle submerged in a highly viscous fluid.

[1] A. Lenshof, et al., *Lab Chip* **12**, 1210 (2012). [2] P. Glynne-Jones, et al., *J. Acoust. Soc. Am.* **133**, 1885 (2013). [3] K. Yosioka and Y. Kawasima, *Acta Acust. united Ac.* **5**, 167 (1955). [4] M. Settnes and H. Bruus, *Phys. Rev. E* **85**, 016327 (2012).

42 Reducing the Superparamagnetic Blocking Temperature of Permalloy Nanomagnets in Artificial Spin Ice Using a Heavy-Metal Interface

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43 Interplay Between Chemical Order and Magnetic Properties in $L1_0$ FeNi Phase (Tetrataenite): A First-Principles

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The high-cost of rare-earth-based permanent magnets has sparked great interest to explore alternative magnetic materials that are free from rare-earth elements. One interesting candidate in this quest is a chemically-ordered $L1_0$ $Fe_{50}Ni_{50}$ phase (tetrataenite) found in iron meteorites. The laboratory synthesis of the ordered phase is hindered because of the slow diffusion of atoms at relatively low order-disorder transition temperature. Since its discovery, several attempts were made to achieve a high degree of chemical order in this alloy. Nevertheless, synthesis of a fully ordered system remains challenging.

Using first-principles-based density-functional theory calculations in combination with Monte Carlo (MC) simulations, we investigate the interplay between chemical order and the magnetic properties of the $L1_0$ FeNi phase. Our results show that the magnetic properties in this alloy are strongly influenced by the degree of chemical order and vice-versa.

44 Hinges for Origami-Inspired Structures by Multi-Material Additive Manufacturing

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Additive manufacturing (AM) of structures capable of changing their properties or shape in a controlled manner is a booming research field. A large number of studies show that the unique capabilities of 4D printing (freedom of geometrical design space and locally controllable material in combination with active materials) enable the development of structures with completely new properties, e.g. programmable mechanical or thermal response and shape transformations. This new way of fabrication is particularly of interest in the field of origami. Origami-inspired structures can be used in deployable structures, where a minimum amount of storage volume is desirable. Conventional fabrication of these structures often requires assembly and joining limiting the achievable designs. This can be overcome by an AM approach.

Seemingly, the only limitation for these newly presented structures is the imagination of the engineer. In reality, structures finding their way into real life applications are an exception. The reason for this gap between laboratory scale and industry are the to-date insufficient mechanical properties.

This study addresses these limitations of 3D printed origami-inspired structures. We focus on the characterization and optimization of the mechanical properties of 3D printed living hinges, including strength, bending stiffness and fatigue. We introduce a new type of 3D printed hinge, fabricated by multi-material FDM printing using continuous fibers. These hinges show large potential to significantly improve the loading capacity of the existing structures. Other hinge designs investigated are multi-material hinges fabricated by ink jet printing of photo-curable polymers and single-material Nylon hinges printed by FDM. The influence of design parameters such as cross-section area and length of the hinge, as well as number of loading cycles, on the mechanical properties are investigated. This work represents a first step towards bringing the advances in the field 3D printed origami-inspired structures closer towards application.

45 Directional Emission of Spin Waves from a Vortex Core

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Spin waves could be used as signal carriers in future spintronic logic and memory devices with a potentially lower power consumption and improved miniaturization compared to the present charge-based CMOS technology [1]. Towards the goal of miniaturization, it was shown recently that isotropically propagating spin waves with ultra-short wavelengths can be generated by exploiting the driven dynamics of topological spin textures such as magnetic vortex cores [2,3]. In this contribution, we show that it is even possible to achieve a directional emission of these waves when a static magnetic field is applied to the vortex structure. This field deforms the vortex core from a point-like source into a curved one-dimensional object, while at the same time displacing it laterally. In particular, self-focusing effects of spin waves can be observed for certain combinations of magnetic field and driving frequency. This directional emission and self-focusing of spin waves from a vortex core opens a way for the directional propagation of spin waves without the need for additional patterning or waveguides.

[1] A. Chumak, et al., *Nat. Phys.* **11**, 453 (2015). [2] S. Wintz, et al., *Nat. Nanotech.* **11**, 948 (2016). [3] G. Dieterle, et al., *Phys. Rev. Lett.* **122**, 117202 (2019).

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